(32 ml.) with sodium nitrite (5.0 g.) 0° and neutralization with a solution of sodium acetate. A deep orange oil separated immediately. After complete addition, when the mixture was brought to room temperature, this oil gradually solidified. The crude product was collected, taken up in ethanol, decolorized with charcoal to give finally bright yellow needles, m.p. 80–81°.

Anal. Calcd. for $C_{14}H_{18}N_2O$: C, 73.02; H, 7.86; N, 12.2. Found: C, 72.49; H, 7.91; N, 12.79.

Cyclization of XIII.—The phenylhydrazone (0.2 g.) was dissolved in absolute ethanol (15 ml.). The solution was cooled in an ice-bath, saturated with dry hydrogen chloride, and then allowed to come to room temperature and remain there for 15 min. Water was added and the resulting precipitate was collected, taken up in methyl alcohol and decolorized with charcoal. On crystallization from 75% aqueous alcohol one obtained 30 mg. of colorless plates, m.p. 183–185°, identical with the compounds obtained by Methods A and B.

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.88; H, 7.09. Found: C, 79.03; H, 7.10.

2-Hydroxy-1,2,3,4,5,6-hexahydrocycloöctindole (XII).—When 200 mg. of the keto compound VI in 5 ml. of tetrahydrofuran was slowly added to an excess of lithium aluminum hydride in 10 ml. of the same solvent, reduction occurred under noticeable warming. The mixture was then refluxed for two hours, decomposed with ice, and extracted with ether. The organic phase was dried over sodium sulfate and left on evaporation 210 mg. of an oil which was obtained from ether solution in colorless needles, m.p. 133° (sintering 128°).

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96. Found: C, 78.35; H, 8.17.

3,4-Cyclohepteno-2-quinolone (XIX).—Condensation of cycloheptanone with ethyl oxalate[28] gave 2-carbethoxycycloheptanone. Condensation with aniline[13,28] yielded cycloheptanone-2-carboxanilide. Cyclization of the anilide with concentrated sulfuric acid gave **XIX**, colorless crystals from ethanol, m.p. 270–271°.

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.90; H, 7.00; N, 6.57.

This compound (XIX) was much more soluble in chloroform than the isomeric (XX),[13] which was obtained by the procedure of Perkin and Plant[28] in colorless needles from 50% aqueous acetic acid, showing a m.p. of 344° and a beautiful deep blue fluorescence in solution, which was not exhibited by the angular compound.

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(28) Ref. 23, p. 531.

CAMBRIDGE, MASS.
BETHESDA, MD.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Isobornylisothiuronium Salts[1]

BY LEE A. SUBLUSKEY[2] AND L. CARROLL KING

Isobornylisothiuronium *p*-toluenesulfonate (VIIa) was prepared from six different terpenes. Evidence is presented to demonstrate (a) that VIIa has the isobornyl structure and that no detectable quantities of a bornylisothiuronium salt or a camphaneisothiuronium salt were formed as by-products, (b) that the enantiomorphic forms of VIIa are capable of racemic compound formation and (c) that the production of VIIa from an optically active terpene is accompanied by some racemization. Optically pure *l*-isobornylisothiuronium *d*-camphorsulfonate and *l*-isobornylisothiuronium iodide were prepared. Isobornyl mercaptan and some of its derivatives were prepared. A discussion of the reactions involved in the formation of VIIa from the various terpenes is given.

Camphene (I) was found to react with thiourea and *p*-toluenesulfonic acid to give isobornylisothiuronium *p*-toluenesulfonate (VIIa). The same salt VIIa was obtained when thiourea and *p*-toluenesulfonic acid were allowed to react with camphene methyl ether (II), tricyclene (III), isobornyl methyl ether (IV) or isoborneol (V), or when thiourea was allowed to react with bornyl *p*-toluenesulfonate (VI).

Treatment of borneol (VIII) with thiourea and *p*-toluenesulfonic acid failed to give VIIa. All attempts to prepare isobornyl *p*-toluenesulfonate, another possible precursor of VIIa, failed.

When prepared from tricyclene, a symmetrical hydrocarbon, the salt VIIa was optically inactive and was obtained in 96% yield, m.p. 182–183°. When VIIa was prepared from camphene ($[\alpha]^{25}D$ 52.7° in methanol) the initial product (VIIa) was obtained in 96% yield, m.p. 160–170°, and $[\alpha]^{24}D$ −21.4°. The melting point of this optically active salt was increased by repeated recrystallization, but by doing this its rotation was decreased to less than $[\alpha]^{25}D$ −2.2°. This is due to separation of a near racemic compound. When the mother liquors from the above recrystallization process were concentrated, an isomeric salt possessing a higher rotation ($[\alpha]^{25}D$ −33.8°) and lower melting point (163–167°) was obtained. These and related observations are summarized in Table I.

TABLE I

Reactant		Crude VIIa				Crystallized VIIa	
Terpene	$[\alpha]^{25}D$	Yield, %	M.p., °C.	$[\alpha]^{25}D$	Racemization,[a] %	M.p., °C.	$[\alpha]^{25}D$
I	52.7°	96	160–170	−21.4°	17[b]	182–183	− 2.20°
						163–167	−33.8°[cd]
II	−3.30°	96	169–174	−3.09°	57[c]	181–183	0°
III	0°	96	182–183	0°	...	182–183	0°
IV	.....	97	177–179	.....	...	181–183	......
V	.....	97	179–181	.....	...	181–183	......
VI	2.04°	85	177–180	−2.52°	43[e]	181–183	0°

[a] % Racemization = $(1 - rA/aB) \times 100$; where A is the rotation of the optically pure reactant used as a standard, B is the rotation of the corresponding optically pure product used as a standard, a is the rotation of the optically impure reactant, and r is the rotation of the partially racemized product. [b] This calculation is based on the highest known rotation for camphene, $[\alpha]^{25}D$ −111° (in methanol). This value was determined in this laboratory using a sample of pure *l*-camphene supplied by J. P. Bain; J. P. Bain and co-workers, THIS JOURNAL, **72**, 3124 (1950). [c] This calculation is based on the value reported for camphene methyl ether, $[\alpha]D$ −12.7°, prepared from camphene, $[\alpha]D$ 50.8°, J. L. Simonsen "The Terpenes," Vol. II, 2nd ed., Cambridge University Press, London, p. 320. [d] Recovered from mother liquors after separation of Racemate VIIa. [e] This calculation is based on the value reported for bornyl *p*-toluenesulfonate, $[\alpha]^{20}D$ 15.5° in alcohol, prepared from borneol, $[\alpha]^{18}D$ 21.0° in alcohol (J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 276 (1912)) taking into account the highest reported value for borneol, $[\alpha]^{20}D$ 34.1° (R. H. Pickard and W. O. Littlebury, *ibid.*, 91, 1973 (1907)).

(1) Presented at the Philadelphia Meeting of The American Chemical Society, April, 1950.

(2) Hercules Powder Company, Wilmington, Delaware.

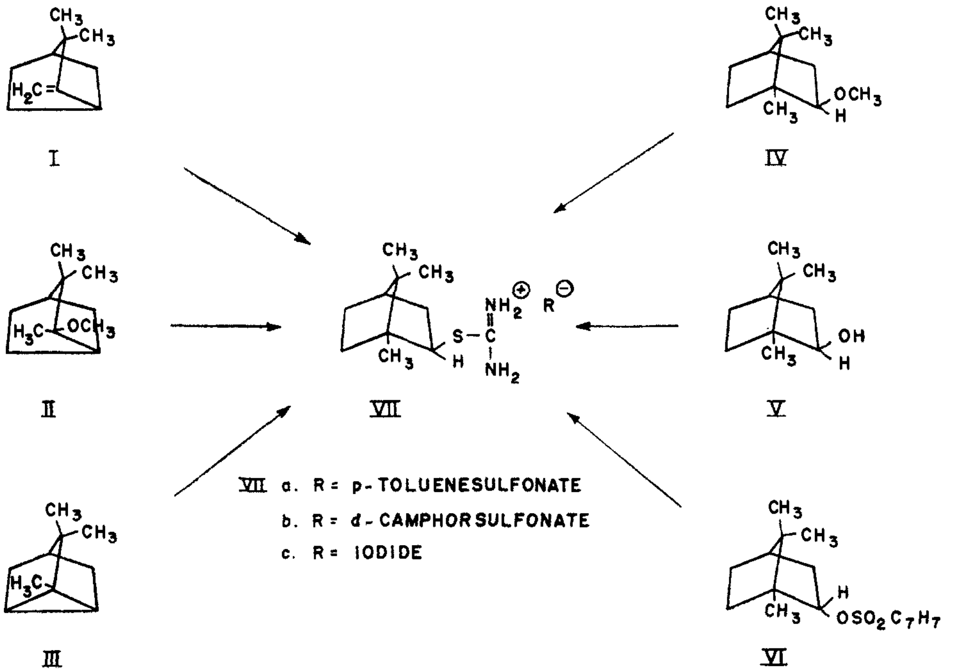

Fig. 1.

Hydrogenolysis[3] of VIIa gave camphane (IX) in isolable yield of 84%. In order to eliminate the possibility of any significant quantities of isocamphane (X), which would result if a camphaneisothiuronium salt (XI) were among the reaction products, the hydrogenolysis was carried out on the crude VIIa prepared from an active camphene ($[\alpha]^{25}\text{D}$ 52.7° in methanol); the optical activity of the crude hydrocarbon so obtained was negligible.

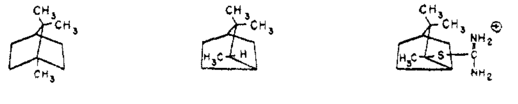

Fig. 2.

The crude salt VIIa, or racemic VIIa, on alkaline cleavage gave the same mercaptan (XII), m.p. 141–141.5°. This mercaptan was further characterized by preparation of the mercury derivative (XIII), m.p. 198–200°, and the disulfide (XIV), m.p. 227–228°. Since these melting points show a marked difference from any of the values reported for bornyl mercaptan and its corresponding derivatives,[4] and since the compound is a camphane derivative (*vida supra*), XII is isobornyl mercaptan.

Since the crude VIIa obtained from optically active camphene is shown to be composed exclusively of components having the camphane structure and the isobornyl configuration it follows that the apparent separation of isomers of VIIa, Table I, is best interpreted as the separation of a racemic modification of VIIa (m.p. 182–183°, $[\alpha]^{25}\text{D}$ less than −2.2°). The lower melting form of VIIa, m.p. 163–167°, $[\alpha]^{25}\text{D}$ −33.8°, results from partial separation of one of the enantiomorphic forms.

Approximately 15% of racemization is associated with the formation of VIIa from optically active terpenes (Table I). This value was calculated from the greatest rotation known for camphene ($[\alpha]^{25}\text{D}$ −111° in methanol)[5] and from the value $[\alpha]^{25}\text{D}$ −54.4° for the pure levo form of VIIa. This latter value was determined from the rotation of the iodide (*l*-VIIc), which was prepared metathetically from *l*-isobornylisothiuronium *d*-camphorsulfonate (*l*-VIIb). *l*-VIIb was obtained from the reaction between camphene, $[\alpha]^{25}\text{D}$ 10°, thiourea and *d*-camphorsulfonic acid, and was separated from its diastereoisomer *d*-isobornylisothiouronium *d*-camphorsulfonate (*d*-VIIb) by fractional recrystallization. To avoid ambiguity due to unlike anion environment, the rotation of *l*-VIIc was determined in the presence of an equimolar quantity of sodium *p*-toluenesulfonate and the rotation of the crude VIIa was determined in the presence of an equimolar quantity of sodium iodide. The validity of these calculations of per cent. racemization rests on the acceptance of two assumptions: (1) the rotations of the enantiomorphic forms of the

Fig. 3.

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(3) The method described by L. C. King and J. A. Campbell, THIS JOURNAL, **71**, 3556 (1949), was used.

(4) E. Rimini, *Gazz. chim. ital.*, **39**, 208 (1909), reports for bornyl mercaptan, m.p. 112°; for mercury salt of bornyl mercaptan, m.p. 175°. J. Haraszti, *J. prakt. Chem.*, **149**, 301 (1937), found for bornyl mercaptan, m.p. 112–113°; mercury salt of bornyl mercaptan, m.p. 175°; bornyl disulfide, m.p. 195°. H. Wuyts, *Ber.*, **36**, 869 (1903). W. Borsche and W. Lange, *ibid.*, **39**, 2351 (1906), and J. Houben and H. Doescher, *ibid.*, **39**, 3506 (1906), claimed bornyl mercaptan to melt in the neighborhood of 60°.

(5) This value was determined on a sample of pure *l*-camphene supplied by Dr. J. P. Bain.

terpenes used as standards represent near optically pure values; and (2) the resolution of *l*-VIIb represents a total resolution.

The extent of racemization calculated from the camphene reaction (17%) is considered to be much more significant than that determined using camphene methyl ether (57%) or that determined using isobornyl *p*-toluenesulfonate (43%). In the latter two cases there is little assurance that the values taken for maximum rotations of the terpene reactants represent near optically pure values.

The observations described in this paper can be visualized by assuming that the reactants I to VI form an ionic species, XV, which in turn reacts with thiourea at C-1 and C-2. Reaction at C-1 by inversion and with displacement of the 1,6-hybrid bond should result in the formation of camphaneisothiuronium salt (XI); however, since this product was not detected it was concluded that reaction at C-1, if it occurs, is reversible. Reaction at C-2 by inversion and with displacement of the 2,6-hybrid bond, on the other hand, would give a single product with the isobornyl structure as observed. Because VIIa, an isobornyl derivative, is the sole product of these reactions it is evident that a carbonium ion of the type XVI, which would suggest formation of some bornyl salt, is of minor importance in directing the course of the reactions.

The racemization observed in the formation of VIIa from optically active terpenes is best explained by assuming a methyl shift from C-7 to C-1,[5a] or by assuming a hydrogen shift from C-6 to C-2.

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Experimental[6]

Preparation of Starting Materials. A. Camphene (I).—An Eastman Kodak Co. practical grade was fractionated with a cut at b.p. 154–155° (740 mm.) being retained; m.p. 47–48°; $[\alpha]^{25}\mathrm{D}$ 10.3° in methanol. A second sample of camphene, m.p. 45–46° and $[\alpha]^{25}\mathrm{D}$ 52.7° in methanol, was used in some experiments.[7] A sample of pure *l*-camphene, $[\alpha]^{25}\mathrm{D}$ −111°, was used for determination of the maximum rotation of camphene.[5]

B. Camphene Methyl Ether (II).—This substance was prepared by the basic methanolysis of camphene hydrochloride according to the directions of Meerwein and Gerard[8]; b.p. 88–89° (17 mm.); f.p. 13°.

C. Tricyclene (III).—The substance was obtained by mercuric oxide oxidation of camphor hydrazone according to the method of Nametkin and Zabrodin[9]; m.p. 65–66° after crystallization from ethanol. A second sample of tricyclene, m.p. 65–66°, was used in some experiments.[10]

D. Isobornyl Methyl Ether (IV).—One hundred grams of camphene and 10 g. of *p*-toluenesulfonic acid monohydrate were refluxed in 300 cc. of methanol for five hours. This solution was then poured into a liter of ice water. The resulting oil was separated, dried over sodium sulfate and fractionated with the cut, b.p. 77.8–79° (17 mm.), being retained.[11]

E. Isoborneol (V).—This substance was prepared from camphene according to the directions of Fisher[12]; m.p. 212–214° (sealed tube).

F. Bornyl *p*-Toluenesulfonate (VI).—This substance was prepared from an Eastman Kodak Co. C.P. grade of borneol (m.p. 206.5–207.5° sealed tube, and $[\alpha]^{25}\mathrm{D}$ 5.72° in methanol) according to the directions of Tipson[13]; $[\alpha]^{23}\mathrm{D}$ 2.04° in methanol; m.p. 78.8–79.4° (sealed tube).

Anal. Calcd. for $C_{17}H_{24}SO_3$: C, 66.20; H, 7.84. Found: C, 66.28; H, 7.85.

Tipson reports this compound to melt at 69°. Ferns and Lapworth[14] prepared it from borneol ($[\alpha]^{18}\mathrm{D}$ 21.0° in alcohol) and reported a melting point of 67°; $[\alpha]^{20}\mathrm{D}$ 15.5° in alcohol. Huckel and Pietrzok[15] used a nearly racemic borneol ($[\alpha]\mathrm{D}$ 4.6°) and reported an inactive ester melting at 80.5°. The difference in these melting points can be explained by racemic compound formation.

Isobornylisothiuronium *p*-Toluenesulfonate (VIIa).—The procedures employed with the various terpene reactants were essentially the same and can be illustrated by the preparation of VIIa from camphene. The results obtained from the preparation of VIIa from all sources are indicated in Table I.

A solution consisting of 1.36 g. (0.01 mole) of camphene ($[\alpha]^{25}\mathrm{D}$ 52.7° in methanol), 3.8 g. (0.02 mole) of *p*-toluenesulfonic acid monohydrate, 3.0 g. (0.04 mole) of thiourea and 10 cc. of ethanol was refluxed for six hours. Upon cooling the solution by the addition of 100 cc. of cold water the salt crystallized. It was collected and leached with 20 cc. of ether; yield 3.7 g. (96%); m.p. 160–170°; $[\alpha]^{24}\mathrm{D}$ −21.4° (in methanol), $[\alpha]^{24}\mathrm{D}$ −21.2° (in methanol containing an equimolar quantity of sodium iodide). Increasing the refluxing time to twenty-four hours had no significant effect on the melting point, rotation or yield of VIIa.

Crystallization of this product several times from water–ethanol or ether–ethanol increased the melting point to 181–183° and lowered the rotation to $[\alpha]^{25}\mathrm{D}$ less than −2.2°.

Anal. Calcd. for $C_{18}H_{28}S_2N_2O_3$: C, 56.22; H, 7.34; N, 7.29. Found: C, 55.88; H, 7.36; N, 7.33.

The preparation of VIIa from VI was carried out by refluxing 3.08 g. (0.01 mole) of VI and 3.0 g. (0.04 mole) of thiourea in 10 cc. of ethanol for ten hours. The product was worked up in the same manner as described above.

Analytical data on the racemic VIIa obtained from all sources were in agreement with the typical example shown. Mixed melting point examination of racemic VIIa from all sources gave no evidence of depression.

Evidence for Racemic Compound Formation between the Enantiomorphs of VIIa.—Recrystallization of VIIa ($[\alpha]^{24}\mathrm{D}$ −21.4°) from ethanol with 25% recovery gave a salt with m.p. 175–178° and $[\alpha]^{25}\mathrm{D}$ −12.1°. Repeated crystallization of this fraction gave the racemate; see above. Addition of excess cold water to the mother liquors from the first crystallization above precipitated a salt with m.p. 170–175° and $[\alpha]^{25}\mathrm{D}$ −26.4°. Recrystallization of this latter salt with 50% recovery gave a salt with m.p. 178–180° and $[\alpha]^{25}\mathrm{D}$ −16.3°, while from the mother liquors of this second recrystallization a salt with m.p. 163–167° and $[\alpha]^{25}\mathrm{D}$ −33.8° was obtained by the addition of water. Treatment of the salt fractions, $[\alpha]^{25}\mathrm{D}$ −12.1° and $[\alpha]^{25}\mathrm{D}$ −33.8°, with ethanolic sodium hydroxide[16] gave the mercaptan (XII), m.p. 140–141°, in yields 76 and 85%, respectively.

Camphane (IX) from the Hydrogenolysis of VIIa.—A slurry consisting of 15 g. (0.039 mole) of VIIa ($[\alpha]^{24}\mathrm{D}$ −21.4°), 250 g. of freshly prepared standard Raney nickel and ethanol, was treated with 1.8 g. (0.045 mole) of sodium

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(5a) This type of shift has been demonstrated on a number of occasions: S. Nametkin and co-workers, *Ann.*, **459**, 144 (1927); *J. prakt. Chem.*, **124**, 144 (1930); **135**, 155 (1932); P. Lipp and G. Stutzinger, *Ber.*, **65**, 243 (1932).

(6) All optical rotation data, unless otherwise stated, were determined on approximately 100 mg. of sample in 3 cc. of solvent using a 1 dcm. tube of 2.5 cc. capacity. All melting points, unless otherwise stated were observed on a Fisher–Johns melting point apparatus. All boiling points are uncorrected.

(7) The authors are indebted to Professor F. N. Hayes of the Illinois Institute of Technology for a sample of this substance.

(8) H. Meerwein and L. Gerard, *Ann.*, **435**, 174 (1924).

(9) S. Nametkin and A. Zabrodin, *ibid.*, **441**, 185 (1925).

(10) The authors are indebted to the Hercules Powder Company for a generous sample of this compound.

(11) H. Meerwin and L. Gerard, ref. 8, reported for isobornyl methyl ether a b.p. 78° (17 mm.).

(12) H. Fisher, "Laboratory Manual of Organic Chemistry," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1934, p. 232.

(13) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(14) J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 276 (1912).

(15) W. Huckel and H. Pietrzok, *Ann.*, **543**, 230 (1940).

(16) Procedure used is described under the preparation of XII.

hydroxide in ethanol. The mixture was stirred and refluxed for ten hours. At the end of this time the nickel was removed by filtration and sufficient cold water was added to separate the hydrocarbon. A 50 cc. dry ether solution containing all of this hydrocarbon exhibited no difference from the instrument's zero reading when an optical rotation measurement was made using a 2 dcm. tube.

The ether solution was boiled down until the terpene began to distill, water and a little ethanol were added and the hydrocarbon was collected; m.p. 149–153°; yield 4.5 g. (84%). Sublimation at atmospheric pressure raised the melting point to 152.5–154° (sealed tube); recrystallization from methanol increased the melting point to 157–158° (sealed tube).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.54; H, 12.91.

Optical rotation measurements made at concentrations of 136 mg. and 250 mg. of hydrocarbon per 3 cc. of methanol in a 1 dcm. tube of 2.5 cc. capacity gave instrument readings of −0.030 and 0.037°, respectively. Camphane, a symmetrical hydrocarbon, has been reported to melt at 153–154° by Simonsen[17] and by Wolff[18] at 156–157°.

The same experiment was carried out on a sample of VIIa (m.p. 182–183, $[\alpha]^{25}\mathrm{D}$ 0°) prepared from tricyclene. The crude hydrocarbon obtained melted at 141–143° (sealed tube). Recrystallization from methanol gave pure camphane, m.p. 156–157° (sealed tube).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.86; H, 12.85.

Isobornyl Mercaptan (XII).—Ten grams (0.059 mole) of VIIa, m.p. 182–183°, $[\alpha]^{25}\mathrm{D}$ 0°, was added to a hot solution consisting of 3.0 g. (0.075 mole) of sodium hydroxide and 100 cc. of ethanol and allowed to reflux for three and one-half hours. The solution was then acidified with glacial acetic acid and diluted with ice-water until it became cloudy. After standing for a few minutes at ice-bath temperatures, the mercaptan was collected and sublimed at 130° and 3 mm.; m.p. 141–141.5° (sealed tube); yield 4.0 g. (90%).

Anal. Calcd. for $C_{10}H_{18}S$: C, 70.51; H, 10.65. Found: C, 71.05; H, 10.07.

This substance is readily oxidized in air and cannot be purified by recrystallization.

The mercaptan was also prepared from VIIa, m.p. 175–178°, $[\alpha]^{25}\mathrm{D}$ −12.1°, and from VIIa, m.p. 163–167°, $[\alpha]^{25}\mathrm{D}$ −33.3°. The melting points of the mercaptans obtained were 139–140° and 137–139°, respectively. The yields were comparable with those obtained from racemic VIIa.

Mercury Salt of Isobornyl Mercaptan (XIII).—When a 50 cc. saturated ethanolic solution of mercuric cyanide was added to 10 g. of XII dissolved in 10 cc. of hot ethanol the mercaptide precipitated immediately. The compound was collected and recrystallized from a large volume of ethanol; m.p. 198–200°.

Anal. Calcd. for $C_{20}H_{34}S_2Hg$: C, 44.54; H, 6.36. Found: C, 44.57; H, 6.21.

Isobornyl Disulfide (XIV).—A solution of 0.5 g. (0.0024 mole) of XII, 0.75 g. (0.0024 mole) of iodine and 10 cc. of a 5% ethanolic sodium hydroxide solution was warmed on a steam-bath for fifteen minutes. After cooling, the product was collected and recrystallized from ethanol; m.p. 227–228.5° (sealed tube); yield 0.44 g. (88%).

Anal. Calcd. for $C_{20}H_{34}S_2$: C, 70.93; H, 10.13. Found: C, 70.73; H, 10.50.

The Diastereoisomeric Salts. A. ***l*-Isobornylisothiuronium *d*-Camphorsulfonate (*l*-VIIb).**—Using 10 g. (0.074 mole) of camphene ($[\alpha]^{25}\mathrm{D}$ 10.3° in methanol), 16 g. (0.21 mole) of thiourea, 20 g. (0.086 mole) of *d*-camphorsulfonic acid (Reychler's, Eastman Kodak, $[\alpha]^{25}\mathrm{D}$ 37.8° in methanol) and 20 cc. of methanol, 27 g. of crude products were obtained after fifteen hours of reacting at reflux temperature followed by the addition of 300 cc. of cold water. A fractional separation of these crude diastereoisomeric salts was achieved by making two water–ethanol and one ether–ethanol recrystallizations. About 11 g. of the more insoluble diastereoisomer was obtained. Seven more water–ethanol recrystallizations gave essentially constant optical measurements: $[\alpha]^{26}\mathrm{D}$ −16.0°, $[\alpha]^{25}\mathrm{D}$ −19.0°, $[\alpha]^{25}\mathrm{D}$ −19.8°, $[\alpha]^{26}\mathrm{D}$ −19.9°, $[\alpha]^{27}\mathrm{D}$ −22.6°, $[\alpha]^{27}\mathrm{D}$ −22.8° in methanol. The melting point of the optically pure salt was 197–198°.

Anal. Calcd. for $C_{21}H_{36}N_2S_2O_4 \cdot H_2O$: C, 54.52; H, 8.28. Found: C, 54.73; H, 8.37.

B. ***d*-Isobornylisothiuronium *d*-Camphorsulfonate (*d*-VIIb).**—By concentration of the mother liquors from the above fractional separation 7 g. of an optically impure but positive rotatory diastereoisomer was isolated. Two recrystallizations from water–ethanol gave $[\alpha]^{28}\mathrm{D}$ 41.3° and $[\alpha]^{26}\mathrm{D}$ 40.6° in methanol and a melting point of 197–200°.

Anal. Calcd. for $C_{21}H_{36}N_2S_2O_4$: C, 56.72; H, 8.16. Found: C, 56.80; H, 8.09.

A mixed melting point of both the negative and positive rotatory salts gave 198–200°.

The Metathetical Conversion of VIIa, *l*-VIIb and *d*-VIIb to *l*-Isobornylisothiuronium Iodide (*l*-VIIc) and *d*-Isobornylisothiuronium Iodide (*d*-VIIc).—The procedure used involved the dissolving of 1 g. of terpene salt in 3 cc. of ethanol in a centrifuge tube, diluting with an equal volume of 47% aqueous hydrogen iodide, cooling for a short time to crystallize the terpene iodide, centrifuging, removing the acid solution and finally washing twice with 3 cc. of cold water. To insure a complete exchange the salt was recycled two more times.

A. ***d,l*-Isobornylisothiuronium Iodide (*d,l*-VIIc) from VIIa.**—This near racemic salt was obtained in an 0.82 g. yield (93%); m.p. darkened 175°, melted 188–191°.

Anal. Calcd. for $C_{11}H_{21}SN_2I$: C, 38.82; H, 6.22. Found: C, 39.03; H, 6.14.

B. ***l*-Isobornylisothiuronium Iodide (*l*-VIIc) from *l*-VIIb.**—This isomer was obtained in a 0.62 g. yield (78%); m.p. darkened 180°, melted 190–193°; $[\alpha]^{25}\mathrm{D}$ −61.4° in methanol, $[\alpha]^{25}\mathrm{D}$ −61.2° in methanol containing equimolar quantity of sodium *p*-toluenesulfonate.

Anal. Found: C, 39.01; H, 6.15.

C. ***d*-Isobornylisothiuronium Iodide (*d*-VIIc) from *d*-VIIb.**—This isomer was obtained in a 0.64 g. yield (81%); m.p. darkened 180°, melted 190–193°; $[\alpha]^{25}\mathrm{D}$ 31.6° in methanol.

Anal. Found: C, 38.94; H, 6.15.

A mixed melting point of *d*-VIIc with *l*-VIIc exhibited no depression.

EVANSTON, ILLINOIS RECEIVED DECEMBER 11, 1950

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[17] J. L. Simonsen, "The Terpenes," Vol. II, Cambridge Press, London, 1932, p. 222.

[18] L. Wolff, *Ann.*, **394**, 86 (1912).