[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Free Radical Addition of Thiolacetic Acid to Some Cyclic Olefins

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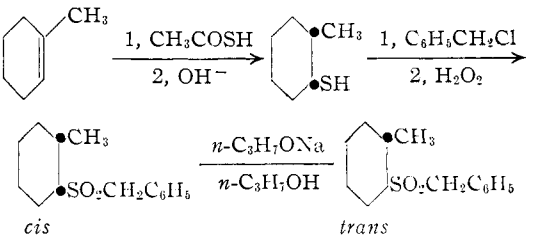
The free radical addition of thiolacetic acid to 1-methylcyclohexene gave about 85% of *cis*- and 15% of *trans*-2-methylcyclohexyl thiolacetate as judged from the composition of the thiol mixture obtained on hydrolysis. Under similar conditions 1-methylcyclopentene gave about 70% of *cis*- and 30% of *trans*-2-methylcyclopentyl thiolacetates. Radical addition of thiophenol to 1-methylcyclohexene also occurred predominantly in a *trans* manner. Addition of thiolacetic acid to camphene, β-pinene and α-pinene appears to have taken place with little or no rearrangement. However, two thiolacetates are formed with each of the pinenes.

As part of a program of synthesis of divalent sulfur compounds it was of interest to study the reaction of thiolacetic acid with several cyclic olefins including 1-methylcyclohexene, 1-methylcyclopentene, camphene, β-pinene and α-pinene.

The first free radical additions of thiolacetic acid to olefins were reported at about the same time by Holmberg[2] and by Ipatieff and Friedman.[3] Since that time similar additions to a large variety of olefins have been reported.[4] In this Laboratory preparation of thiolacetates has been found to provide an excellent general synthetic route to pure thiols, since yields are normally high and orientation is exclusively anti-Markownikoff.[5]

Addition of thiolacetic acid to 1-methylcyclohexene and 1-methylcyclopentene was of interest in connection with the stereoselectivity of free radical addition reactions, as well as for the preparation of the thiols. Cunneen[4b] reported the addition of thiolacetic acid to 1-methylcyclohexene, but did not attempt to decide the stereorelationships of the groups in the product. In the present work the additions were initiated at ordinary temperatures with the aid of light. Excellent yields of thiolacetates were obtained from 1-methylcyclohexene and from 1-methylcyclopentene. These were hydrolyzed with aqueous alcoholic alkali to the thiols. The crude thiols were converted to the corresponding benzyl sulfides and these were oxidized to the sulfones, which were purified by fractional crystallization. In each instance the sulfone formed could be isomerized almost completely by heating with sodium propoxide in *n*-propyl alcohol solution. It seems reasonable to suppose that the original sulfone had the *cis* structure, and was isomerized, by way of the carbanion, to the more stable *trans* isomer on heating with alkali. The sequence of reactions is shown for 1-methylcyclohexene.



Careful fractional distillation[6] separated each thiol into two fractions. For 2-methylcyclohexanethiol 17% of a lower boiling and 83% of a higher boiling fraction were collected. For 2-methylcyclopentanethiol the percentages of the lower and higher boiling materials were 29 and 71%.

The lower boiling 2-methylcyclohexanethiol and 2-methylcyclopentanethiol in each instance gave the more stable benzyl sulfone derivative. The higher boiling thiol was in each instance converted to the less stable benzyl sulfone, identical with that prepared from the crude thiol sample. It is clear, then, that thiolacetic acid gives predominantly *cis*-2-methylcyclohexyl and *cis*-2-methylcyclopentyl thiolacetates (*trans*-addition), but that this is by no means the exclusive product.

Allinger[7] in a restatement of von Auwers' rule states with respect to *cis* and *trans* isomers in cyclic systems: "That isomer which has the higher boiling point, higher index of refraction and higher density is the isomer which possesses the least stable configuration." Our assignment of *cis* and *trans* structures is consistent with this modified von Auwers rule.

Cunneen[4b] reported the addition of thiophenol to 1-methylcyclohexene and oxidation of the resulting sulfide to a sulfone. Reaction of *cis*-2-methylcyclohexanethiol with iodobenzene and oxidation of the resulting sulfide gave a sulfone identical with that prepared by the method of Cunneen. This sulfone was isomerized by heating with sodium propoxide in propyl alcohol, which indicates a *cis* structure. Therefore, thiophenol also adds to 1-methylcyclohexene primarily by *trans* addition.

Goering, Abell and Aycock[8] were first to observe that free radical addition to 1-substituted cyclohexenes occurs by stereoselective *trans* addition. They reported that free radical addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene was completely stereoselective (*i.e.*, stereospecific), and interpreted these data in terms of a bridged free radical intermediate. Our present results, which were announced several years

(1) American Petroleum Institute Project 48B Fellow, 1951–1953; Procter and Gamble Fellow, 1953–1954.

(2) B. Holmberg, *Arkiv. Kemi, Mineral Geol.*, **12B**, No. 47, 3 (1938).

(3) V. N. Ipatieff and B. S. Friedman, THIS JOURNAL, **61**, 71 (1939).

(4) (a) B. Holmberg and E. Schjanberg, *Arkiv. Kemi, Mineral. Geol.*, **14A**, No. 7 (1940); (b) J. I. Cunneen, *J. Chem. Soc.*, 134 (1947); (c) H. Behringer, *Ann.*, **564**, 219 (1949); (d) R. Brown, W. E. Jones and A. R. Pinder, *J. Chem. Soc.*, 2123 (1951).

(5) W. A. Hewett, Ph.D. Dissertation, Northwestern University, August, 1955.

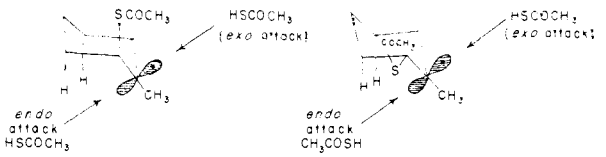
(6) We wish to thank W. E. Haines and his co-workers at the Bureau of Mines, Laramie, Wyoming, for carrying out these fractionations.

(7) N. L. Allinger, *Experientia*, **10**, 328 (1954).

(8) H. L. Goering, P. L. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

ago,[9] showed that the radical addition of thiolacetic acid to such systems is not stereospecific, since some *cis* addition occurs. This indicated that the concept of a bridged radical intermediate would not provide an entirely satisfactory explanation of the course of such additions. Recently Goering, Relyea and Larsen[10] have reported other examples of radical additions of this type which are not stereospecific. They have found that the degree of stereoselectivity increases with increased concentration for the addition of hydrogen sulfide, and varies with the reagent in the order thiophenol > hydrogen sulfide > thiolacetic acid. These results and other considerations led to an alternative representation to explain the predominant *trans* addition.[10,11]

Goering[10] suggests that if in the initial radical attack the incoming group (*e.g.*, CH_3COS–) assumes an axial position, the trigonal carbon will be shielded from attack on that side, and that this will lead to a *cis* product. Although it is not specifically stated in the paper, the representation given by Goering[10] implies a planar configuration, for the trigonal carbon. In terms of the diagram shown this would amount to *endo* attack by CH_3COSH on Ia. However, if a planar configuration is assumed for this carbon in the free radical inter-

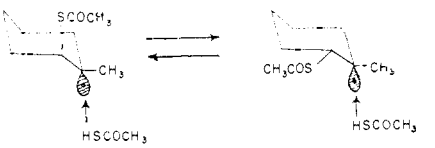


Ia Ib

Planar free radical intermediate

mediate, it does not necessarily follow that *endo* attack on Ia would be preferred. A closely analogous situation exists in the ketonization of enols, and here Zimmerman[12] has shown that due to the hindrance effect of the β-hydrogens (shown in Ia and Ib) *endo* attack of an acid HA is prohibited in an intermediate like Ib ($SCOCH_3$ equatorial). With the $SCOCH_3$ group axial (Ia) *exo* attack becomes less likely, but examination of models indicates that, unless it is assumed that the $SCOCH_3$ group is rotated so as to provide maximum hindrance, *exo* attack may still be favored over *endo*. If this is the correct picture, the *cis* product (predominant) would arise from *exo* attack on Ib rather than *endo* attack on Ia. It is difficult to account for the change in stereoselectivity with changing concentration[11] on this basis, however.

It is not at all certain that the carbon atom holding the odd electron does not maintain a tetrahedral rather than assume a planar configuration. If this carbon is tetrahedral the reaction would be represented as in IIa or IIb rather than as in Ia or Ib. If the methyl group assumes an equatorial



IIa IIb

Tetrahedral free radical intermediate

position, as seems logical, formation of the *cis* isomer would result from attack on IIa. The predominant, but not exclusive, *trans* radical additions to these systems would then be explained by assuming that the $-SCOCH_3$ group initially takes an axial position (IIa) and that conversion to IIb may occur to some extent. Steric hindrance to attack of CH_3COSH would not play an important role according to this mechanism. Increased stereoselectivity with increasing concentration[10] could result from less conversion of IIa to IIb.

No clear-cut choice between the mechanisms illustrated appears to be possible at present. A bridged radical intermediate[8] in these additions is made highly unlikely, however, by the failure of radical addition in non-cyclic alkenes to occur by stereoselective paths.[13]

The reactions of thiolacetic acid with camphene, β-pinene and α-pinene were carried out primarily to see whether or not free radical type rearrangements occur in these systems, which are notorious for their ease of carbonium ion rearrangements. Rearrangements during free radical additions are rare, one of the few well-established examples occurring in the addition of carbon tetrachloride to β-pinene.[14] Addition of thiolacetic acid to camphene followed by hydrolysis gave an over-all yield of 64% of a thiol, which appeared to be a single compound. Desulfurization yielded isocamphane, which indicates that no rearrangement occurred.

Addition of thiolacetic acid to β-pinene and hydrolysis gave a mixture of two thiols, as indicated by the isolation of two 2,4-dinitrophenyl sulfide derivatives. However, the original thiol mixture showed no band at 12.5 μ (characteristic of the olefinic band of Δ^1-*p*-menthene), which would be present if rearrangement of the type previously observed[14] had occurred (to give III). Infrared bands characteristic of norpinane were present, and it seems likely that no rearrangement of the carbon skeleton to III took place. The two thiols are probably *cis–trans* isomers (comparable to I and II) which are formed as a result of a partially stereoselective addition, as with 1-methylcyclohexene (I–III).

The infrared spectra of the 2,4-dinitrophenyl sulfide derivatives of these thiols were nearly identical, which shows a very close structural relationship. Addition of thiolacetic acid to α-pinene and hydrolysis also gave two thiols, as indicated by isolation of two 2,4-dinitrophenyl sulfide derivatives. These also are believed to be *cis–trans* isomers.

(9) F. G. Bordwell and W. A. Hewett, Abs. 126th Meeting of the Am. Chem. Soc., New York, N. Y., September, 1954, p. 6-O.

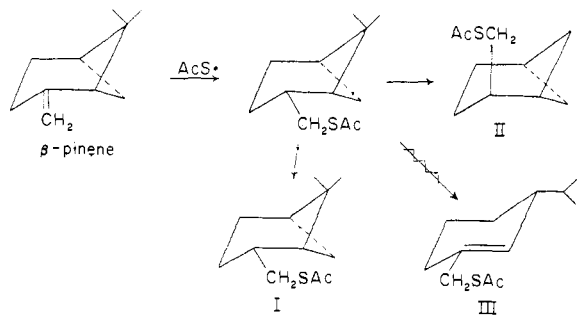
(10) H. L. Goering, D. I. Relyea and D. W. Larsen, THIS JOURNAL, **78**, 348 (1956).

(11) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

(12) H. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955); H. Zimmerman, THIS JOURNAL, **78**, 1168 (1956). Zimmerman suggests use of the terms "*endo*" and "*exo*" attack.

(13) P. S. Skell and R. C. Woodworth, THIS JOURNAL, **77**, 4638 (1955); F. G. Bordwell and N. P. Neureiter, Abstracts of Miami Meeting of the American Chem. Soc., April, 1957.

(14) (a) D. M. Oldroyd, G. S. Fisher and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950); (b) G. du Pont, R. Dulon and G. Clement, *Bull. soc. chim.*, 1056 (1950).



It has been shown by Seubold[15] that the life time of a radical under a particular set of conditions is an important factor in determining whether or not it will rearrange. The absence of rearrangement may be due to a very short half-life for the intermediate free radical. In this connection it is also of interest that carbon tetrachloride does not enter into the free radical chain of this type addition reaction, since chlorine was not incorporated into the product in an addition carried out in carbon tetrachloride solution, even when the ratio of carbon tetrachloride to thiolacetic acid was ten to one.

Experimental[16]

cis- **and** *trans*-**2-Methylcyclohexanethiols.**—2-Methylcyclohexyl thiolacetate was prepared by slowly adding 156 g. (2.0 moles) of practical grade thiolacetic acid to 164 g. (1.7 moles) of 1-methylcyclohexene while irradiating with a 100 watt bulb. Care must be taken as the reaction is highly exothermic and may have an induction period of several minutes. Distillation gave 250 g. (85%) of product, b.p. 110° (14 mm.), $n^{25}D$ 1.495. The reported boiling point of 2-methylcyclohexyl thiolacetate is 110° (14 mm.).[4b] (The thiolacetate is a mixture of *cis* and *trans* isomers.)

The thiolacetate (246 g., 1.43 moles) was hydrolyzed by refluxing for one hour in 2 l. of 10% aqueous alcoholic (50% by volume) potassium hydroxide. The solution was neutralized with glacial acetic acid and the non-aqueous phase separated. The aqueous portion was extracted three times with pentane and the pentane extracts were dried over anhydrous magnesium sulfate. The combined non-aqueous phase and pentane extracts were distilled giving 155 g. (82%) of 2-methylcyclohexanethiol, b.p. 71–72° (23 mm.); a b.p. of 165° was reported.[4b]

Careful fractionation[6] gave 16% of the charge as a fraction (*trans* isomer) boiling at 138.7° (300 mm.), $n^{20}D$ 1.4851, and 76% of the charge as a fraction (*cis* isomer) boiling at 143.4° (300 mm.), $n^{20}D$ 1.4937. Ignoring intermediate cuts the percentage of *trans* and *cis* isomers based on 92% of the charge are 17% and 83%, respectively.

The 2,4-dinitrophenyl sulfide derivatives of the pure thiols were prepared in the usual manner.[17]

Recrystallization of the derivative from the lower boiling fraction gave *trans*-**2-methylcyclohexyl 2,4-dinitrophenyl sulfide,** m.p. 140–140.5°.

Anal. Calcd for $C_{13}H_{16}O_4N_2S$: C, 52.69; H, 5.44. Found: C, 52.32; H, 5.65.

Recrystallization of the derivative from the higher boiling fraction gave *cis*-**2-methylcyclohexyl 2,4-dinitrophenyl sulfide,** m.p. 100–100.5°. This derivative also was obtained from the crude thiol prior to fractionation.

Anal. Calcd. for $C_{13}H_{16}O_4N_2S$: C, 52.69; H, 5.44. Found: C, 52.31; H, 5.31.

cis-**2-Methylcyclohexyl Benzyl Sulfone.**—The benzyl sulfide was prepared by dissolving the higher boiling thiol in 95% alcohol containing an equimolar quantity of sodium hydroxide and treating with an equimolar quantity of benzyl chloride. The solution was poured into water and the sulfide obtained by extraction with pentane. Oxidation of the crude sulfide, obtained by evaporation of the pentane, with a sixfold excess of 30% hydrogen peroxide in glacial acetic acid followed by addition of the reaction mixture to water gave the crude benzyl sulfone in 72% yield. One recrystallization from glacial acetic acid gave *cis*-**2-methylcyclohexyl benzyl sulfone,** m.p. 74–74.5°.

Anal. Calcd. for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99. Found: C, 66.50; H, 7.74.

This benzyl sulfone was also obtained from the thiol mixture prior to fractionation, but the melting point of the crude sulfone was low (58–65°), and repeated recrystallizations were necessary to raise the melting point to that of the pure *cis*-sulfone.

Isomerization of *cis*-**2-Methylcyclohexyl Benzyl Sulfone.**—The *cis*-sulfone (5.0 g., 0.02 mole) was dissolved in a solution of 1.6 g. (0.02 mole) of sodium *n*-propoxide in 30 ml. of *n*-propyl alcohol, and the solution was refluxed for 44 hr. The solution was diluted with 150 ml. of water and neutralized with dilute hydrochloric acid. The oil which separated was induced to crystallize by cooling with Dry Ice. After several recrystallizations from glacial acetic acid *trans*-**2-methylcyclohexyl benzyl sulfone** melting at 84–84.5° was obtained. A mixture with the *cis*-sulfone melted at 47–57°.

Anal. Calcd. for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99. Found: C, 66.57; H, 7.98.

The *trans*-sulfone also was obtained starting with the lower boiling thiol fraction using the method described above for the *cis*-sulfone.

2-Methylcyclopentyl Thiolacetate.—Starting with 1.9 moles of 1-methylcyclopentene and 2.1 moles of practical grade thiolacetic acid, 240 g. (80%) of 2-methylcyclopentyl thiolacetate, b.p. 98–101° (25 mm.), $n^{25}D$ 1.4900, was obtained by the procedure described above. This is a mixture of *cis* and *trans* isomers.

Anal. Calcd. for $C_8H_{14}OS$: C, 60.71; H, 8.92. Found: C, 61.05; H, 9.01.

cis- **and** *trans*-**2-Methylcyclopentanethiols.**—Hydrolysis of the thiolacetate as described above gave a mixture of *cis-* and *trans*-thiols in 96% yield, b.p. 146–148°.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41. Found: C, 62.37; H, 10.32.

Careful fractional distillation[6] gave 27% of the charge as a lower boiling fraction (*trans* isomer), b.p. 135.8° (590 mm.), $n^{20}D$ 1.4783, and 65% as a higher boiling fraction (*cis* isomer), b.p. 142.5° (590 mm.), $n^{20}D$ 1.4884. Based on 92% of the charge, 29% of *trans* isomer and 71% of *cis* isomer were obtained.

trans-**2-Methylcyclopentyl 2,4-dinitrophenyl sulfide,** prepared from the lower boiling fraction,[17] melted at 112.5–113° after crystallization from absolute alcohol.

Anal. Calcd. for $C_{12}H_{14}O_4N_2S$: C, 51.05; H, 5.00. Found: C, 51.02; H, 5.00.

cis-**2-Methylcyclopentyl 2,4-dinitrophenyl sulfide,** prepared from the higher boiling fraction,[17] melted at 99–100° after crystallization from absolute alcohol.

Anal. Calcd. for $C_{12}H_{14}O_4N_2S$: C, 51.05; H, 5.00; N, 9.93. Found: C, 50.52; H, 4.82; N, 10.02.

The 2,4-dinitrophenyl sulfide derivatives prepared from the thiol before fractionation melted at ranges between 70–90° despite repeated crystallizations from hexane. Carbon and hydrogen analysis of this mixture checked the theoretical for $C_{12}H_{14}O_4N_2S$, supporting the view that it is a mixture of the derivatives of the *cis-* and *trans*-thiols.

cis- **and** *trans*-**2-Methylcyclopentyl Benzyl Sulfones.**—These sulfones were prepared by the general method described above starting with the pure thiols. The *cis* isomer melted at 74.5–75° after crystallization from aqueous methanol or hexane.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.51; H, 761. Found: C, 65.71; H, 7.41.

The *trans* isomer melted at 101–101.5° after recrystallization from methanol.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.75; H, 7.42.

The crude thiol mixture yielded a benzyl sulfone which was purified only with difficulty. Repeated recrystallizations

(15) F. H. Seubold, Jr., THIS JOURNAL, **75**, 2532 (1953).

(16) Microanalyses were by Miss Hilda Beck.

(17) R. W. Bost, J. O. Turner and R. D. Morton, THIS JOURNAL, **54**, 1985 (1932).

from glacial acetic acid gave material melting sharply at 61–62°, but several additional recrystallizations from methanol gave the pure *cis* isomer, m.p. 74–74.5°. Carbon and hydrogen analysis of the material melting at 61–62° supported the conclusion that it was a mixture of *cis*- and *trans*-benzyl sulfones. A mixture of the *cis*- and *trans*-sulfones melted at 62–76°.

Isomerization of *cis*-2-Methylpentyl Benzyl Sulfone.—Treatment of either the pure *cis*-benzyl sulfone or the mixture of benzyl sulfones melting at 61–62° according to the method used to isomerize *cis*-2-methylcyclohexyl benzyl sulfone gave a 91% conversion to the *trans*-sulfone, m.p. 98–100°.

Attempts to isomerize the *cis*-thiol or *cis*-benzyl sulfide by this procedure were unsuccessful.

***cis*- and *trans*-2-Methylcyclohexyl Phenyl Sulfones.**—*cis*-2-Methylcyclohexylphenyl sulfide was prepared by heating a mixture of *cis*-2-methylcyclohexanethiol with iodobenzene and copper powder at 220° according to the procedure described by Cunneen.[4b] The sulfide also was prepared in 50% yield from 1-methylcyclohexene and thiophenol by heating on the steam-bath in the presence of *t*-butyl peroxide. Oxidation of each of these samples with 30% hydrogen peroxide in glacial acetic acid gave the same sulfone, m.p. 107–108° after recrystallization from methanol; Cunneen[4b] reports the melting point as 108°. Isomerization of the sulfone by the method described above gave an 85% yield of ***trans*-2-methylcyclohexyl phenyl sulfone** (m.p. 82–86°), which melted at 90–90.5° after recrystallization from methanol.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.40; H, 7.30.

A mixture of the *cis*- and *trans*-sulfones melted at 88–95°.

Addition of Thiolacetic Acid to 1-Hexene in Carbon Tetrachloride Solution.—Thiolacetic acid (28 g., 0.3 mole) was added slowly to a solution of 25 g. (0.3 mole) of 1-hexene in 461.5 g. (3 moles) of carbon tetrachloride under irradiation. The yield of *n*-hexyl thiolacetate, b.p. 88° (13 mm.), $n^{25}D$ 1.4591, was 83%; Wenzel and Reid[18] reported b.p. 205.8° (760 mm.), $n^{25}D$ 1.4591.

2-Mercaptomethyl-3,3-dimethylbicyclo[2,2,1]heptane.—Addition of 90 g. (1.2 moles) of thiolacetic acid to 136 g. (1 mole) of camphene in the usual manner gave 164 g. (77%) of 2-(S-thiolacetoxymethyl)-3,3-dimethylbicyclo[2,2,1]heptane, b.p. 93–95° (0.8–1.0 mm.); Behringer[4c] reports a boiling point of 147–148° (14 mm.). Alkaline hydrolysis gave 109 g. (83%) of 2-mercaptomethyl-3,3-dimethylbicyclo[2,2,1]heptane, b.p. 116° (20 mm.).

Anal. Calcd. for $C_{10}H_{18}S$: C, 70.52; H, 10.65. Found: C, 70.68; H, 10.64.

The 2,4-dinitrophenyl sulfide[17] of this thiol melted at 126–126.5° after crystallization from alcohol.

Anal. Calcd. for $C_{16}H_{20}O_4N_2S$: N, 8.33. Found: N, 8.33.

Isocamphane from the Desulfurization of 2-Mercaptomethyl-3,3-dimethylbicyclo[2,2,1]heptane.—Following the procedure of Papa, Schwenk and Ginsberg[19] a solution of 20 g. (0.117 mole) of thiol in 500 ml. of 10% aqueous sodium hydroxide and 40 ml. of alcohol was heated and stirred vigorously on a steam-bath for two hours, during which time 40 g. of Raney nickel alloy was added to the solution in small increments. The reaction mixture was heated an additional two hours and the product accumulating in the condenser during this time was washed back into the reaction flask with a little alcohol. The mixture was then steam distilled, and the distillate extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate, and then distilled through a 3-plate Vigreux column to yield 3.5 g. (22%) of isocamphane, b.p. 163–164°, m.p. 54–56°. The reported physical constants[20] are b.p. 164.5° and m.p. 65–66° (the expected rearrangement product, camphane, boils at 160–161° and melts at 156–156.5°[20]).

The Addition of Thiolacetic Acid to β-Pinene.—The addition of 25.4 g. (0.33 mole) of freshly distilled thiolacetic acid to 45 g. (0.33 mole) of β-pinene gave 59 g. (84%) of thiolacetate, b.p. 91–92° (0.5 mm.), $n^{25}D$ 1.5090.

Anal. Calcd. for $C_{12}H_{20}OS$: C, 67.87; H, 9.49. Found: C, 68.00; H, 9.44.

Hydrolysis of 53 g. (0.25 mole) of the thiolester gave 40 g. (94%) of thiol, b.p. 124–125° (25 mm.), $n^{25}D$ 1.5100.

Anal. Calcd. for $C_{10}H_{18}S$: C, 70.52; H, 10.65. Found: C, 70.86; H, 10.52.

Neither the thiolacetate nor the thiol showed a band in the 12.5 μ region of the spectra, which indicates the absence of a RR'C=CHR'' type of double bond.

Recrystallization of the 2,4-dinitrophenyl sulfide derivative of the thiol from alcohol gave two different products. The first crop of crystals (compound A) melted at 141–143°, and this melting point was not changed by recrystallization from hexane. The second crop of crystals (compound B) melted at 121–122°, and recrystallization from alcohol did not raise the melting point. A mixture of the derivatives melted at 118–130°.

Anal. Calcd. for $C_{16}H_{20}O_4N_2S$: N, 8.33. Found: N, 8.40 (for A); N, 8.45 (for B).

Addition of Thiolacetic Acid to α-Pinene.—Addition of 22.8 g. (0.3 mole) of freshly distilled thiolacetic acid to 41 g. (0.3 mole) of α-pinene gave 43 g. (70%) of thiolacetate, b.p. 105° (3.2 mm.); Behringer[4c] reported the b.p. to be 135–137° (13 mm.). Hydrolysis of 42 g. of the thiolacetate gave 22 g. (64%) of thiol, b.p. 84° (7 mm.).

Anal. Calcd. for $C_{10}H_{18}S$: S, 70.52; H, 10.65. Found: C, 70.79; H, 11.07.

Crystallization of the 2,4-dinitrophenyl sulfide derivative[17] from alcohol gave two different products. The first crop (compound A') melted at 154–160°, and recrystallization from hexane gave material melting at 158.5–164°. The second crop (compound B') melted at 143–145°, and recrystallization from alcohol raised the melting point to 146–148°. A mixture of the two derivatives melted at 138–161°.

Anal. Calcd. for $C_{16}H_{20}O_4N_2S$: N, 8.33. Found: N, 8.40 (for A'); N, 8.53 (for B').

Exhaustive attempts to purify the derivatives A, B, A' and B' were not made. It is probable that some or all might have higher melting points when purified further. A mixture of A (m.p. 141–143°) and B' (146–148°) melted at 115–130°.

EVANSTON, ILLINOIS

(18) F. W. Wenzel and E. E. Reid, THIS JOURNAL, **59**, 1089 (1937).

(19) D. Papa, R. Schwenk and H. F. Ginsberg, *J. Org. Chem.* **14**, 723 (1949).

(20) J. L. Simonsen and I. N. Owen, "The Terpenes" (second edition), The University Press, Cambridge, England, Vol. 2, 1949, p. 272.

[CONTRIBUTION FROM THE RESEARCH AND BIOLOGICAL LABORATORIES OF AYERST, MCKENNA & HARRISON LIMITED]

New Analeptics. 1-Benzhydryl-2-alkyl-2-thiopseudoureas[1]

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The synthesis of a series of S-alkylated benzhydrylthioureas is reported. The lower members have shown analeptic properties.

During a search for new spasmolytic agents, 1-benzhydryl-2-methyl-2-thiopseudourea hydroiodide (I) was prepared. When tested in animals this compound showed an interesting central stim-

(1) This paper was presented before the Division of Medicinal Chemistry, American Chemical Society, Miami, Florida, April, 1957.