which the reaction was examined only by means of the e.s.r. signal, samples of 2–3-mg. size were used. The alkali metals, except for lithium, were distilled into the sample tubes under a vacuum of about $10^{-6}$ torr; lithium metal was carefully melted (with partial reaction with the glass) in a side-arm tube.

**Cleavage of β-Naphthyl Ether.**—As a typical example, the cleavage by sodium and subsequent work-up of β-naphthyl ether is described. After introduction of β-naphthyl ether (1.00 g., 0.0037 mole) into the sample tube, the system was outgassed and a small chunk (*ca.* 0.2 g.) of freshly cut sodium was distilled three times through constrictions in a side tube, each constriction being sealed off after use. About 4 cc. of dimethoxyethane was distilled into the sample tube (using liquid nitrogen as coolant), and the sample and solvent were thoroughly degassed. The sample tube was then sealed from the vacuum system and shaken two or three times to allow the solution to contact the metal mirror. An orange color immediately developed, which was found to be the color of the mononegative ion. Subsequent shaking caused the mixture to turn a dark blue-green, indicative of the formation of naphthalene negative ion. The mixture was shaken 1 hr. longer, and the sample tube was broken open and the contents exposed to air, whereupon the blue-green color rapidly disappeared. The mixture was neutralized with dilute sulfuric acid and 20 cc. of ether added to it. Extraction of the products was accomplished, first with sodium bicarbonate solution, then with sodium hydroxide, the neutral material remaining unchanged. The acidified bicarbonate extract in this case, as in all others, yielded only a very thin film (after evaporation of the ether solvent) having an odor of aliphatic acids. The acidified sodium bicarbonate extract yielded a white material, which, after sublimation, weighed 0.30 g., m.p. 122°. The melting point upon admixture with authentic β-naphthol was unchanged; yield, 56%. The ether was removed from the neutral material, which was fractionally sublimed. The first and easiest obtained fractions were of an aromatic white material, 0.20 g., m.p. 80–83°, mixture melting point with authentic naphthalene unchanged. Subsequent fractions yielded a white compound, 0.13 g., m.p. 181–183.5 (mixture melting point with β-dinaphthyl unchanged), and a small amount (0.01 g.) of very high-melting material which was not identified. We assume some product loss occurred during the work-up and sublimation procedure; the product yields are all based on pure material recovered.

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## The Conversion of 2-Acetoxypulegone to Menthofuran. Terpenes. V.[1]

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Menthofuran, II, has been prepared from isopulegone, I, and from pulegone, Ia, as shown in Diagram I.[4,5,6]

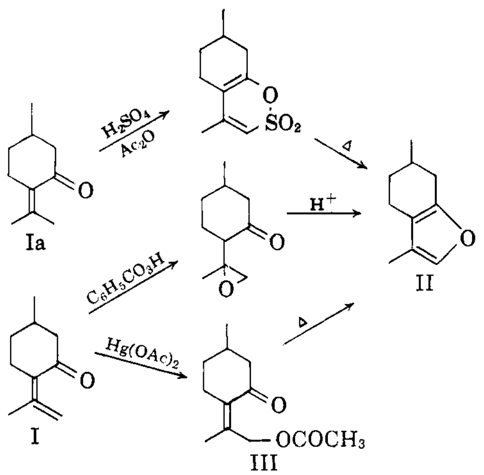
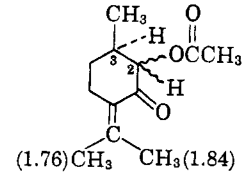


DIAGRAM I

We now report the isolation of optically pure menthofuran as the major product of the pyrolysis of 2-acetoxypulegone, V (Diagram 2). This unusual reaction prompted us to reinvestigate the structure of the product obtained by treating pulegone with mercuric acetate; structure V was assigned to this product by earlier workers.[7] Structure III previously had been assigned to the product obtained by treating isopulegone with mercuric acetate; on pyrolysis III gave menthofuran.

The product isolated on treatment of pulegone with mercuric acetate according to the procedure of Reitsema[7b] was found to have physical properties identical with those previously reported. However, gas chromatography (hydrogen flame detector) showed that it was a mixture containing approximately equal amounts of two components; attempts to separate these two compounds using column chromatography failed. Nevertheless, an examination of the n.m.r. spectrum of the product showed that III was not one of these components, and that the mixture consisted of the *cis* and *trans* isomers of 2-acetoxypulegone, V. The methyl protons of the isopropylidene group in V (*cis* and *trans* isomers) appeared at δ 1.76 (3 protons) and at δ 1.84 (3 protons). In both the *cis* and *trans* isomers the methyl protons of the isopropylidene group *cis* to the carbonyl group would be expected to show a paramagnetic shift compared with the methyl protons *trans* to the carbonyl group (see Diagram 2).[8] Structure III would be expected to show only three protons in this region of its n.m.r. spectrum. The protons of the C-3 methyl group in V ap-



Va *cis* (acetoxy group up)
$CH_3$ at $C_3$: δ 0.96; doublet $J = 7$ c.p.s.
H at $C_2$: δ 5.10; doublet, $J = 5.5$ c.p.s.
Vb *trans* (acetoxy group down)
$CH_3$ at $C_3$: δ 1.05; doublet $J = 5.5$ c.p.s.
H at $C_2$: δ 4.64; doublet $J = 10.5$ c.p.s.

DIAGRAM 2.—Position (δ) of protons in n.m.r. spectrum of 2-acetoxypulegone.

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[1] Terpenes. IV. Constitution and Absolute Configuration of Eremophilenolide, *Tetrahedron*, in press. Terpenes. III, *Chem. Ind.* (London), 38 (1962). Terpenes. II, *J. Org. Chem.*, **27**, 3535 (1962). Terpenes. I, *ibid.*, **26**, 981 (1961).

[2] Holder of National Science Foundation Summer Fellowship for Graduate Teaching Assistants, Summer, 1962. National Institutes of Health Fellow, 1962–63.

[3] Participant in National Science Foundation College Chemistry Teachers Research Participation Program at Oklahoma State University, Summer, 1962.

[4] W. Treibs, *Ber.*, **70**, 85 (1937).

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[7] (a) W. Treibs and H. Bast, *ibid.*, **561**, 165 (1949); (b) R. H. Reitsema, *J. Am. Chem. Soc.*, **79**, 4465 (1957).

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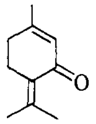
peared as a pair of doublets. The *cis* isomer, Va (see Diagram 2), showed a doublet centered at δ 0.96 ($J$ = 7 c.p.s., 1.8 protons), whereas the *trans* isomer, Vb, showed a doublet centered at δ 1.05 ($J$ = 5.5 c.p.s., 1.2 protons). The proton at C-2 in the *cis* isomer appeared as a doublet centered at δ 5.10 ($J$ = 5.5 c.p.s., 0.6 proton) whereas in the *trans* isomer it appeared as a doublet centered at δ 4.64 ($J$ = 10.5 c.p.s., 0.4 proton). The coupling constants of *cis* 1,2 protons are known to be smaller than the corresponding *trans* isomers.[8] For structure III, one would expect an unsplit signal corresponding to two protons in this region of the n.m.r. spectrum.

Pyrolysis of the mixture of *cis*- and *trans*-2-acetoxypulegone gave essentially optically pure menthofuran, II, in 43% yield. The optical purity of the menthofuran shows that the reaction could not have proceeded *via* intermediate VI, the expected pyrolysis product.



VI

Examination of Dreiding models indicated that in *trans*-2-acetoxypulegone with the cyclohexane ring in a boat conformation, and in *cis*-2-acetoxypulegone with the cyclohexane ring in a chair conformation, the carbonyl group of the acetoxy group can be in close proximity to the hydrogen atoms of one of the methyl groups of the isopropylidene substituent. In the *trans* isomer, this carbonyl can actually approach a hydrogen atom of the isopropylidene group more closely than it can approach the *cis* hydrogen atom at C-3. The route shown in Diagram 3 is suggested.[9]

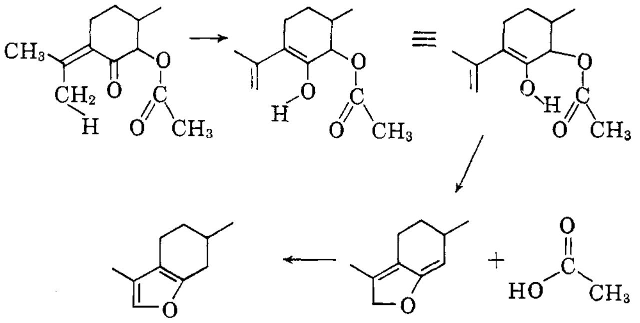


DIAGRAM 3

In view of our findings we decided to repeat the reaction of isopulegone with mercuric acetate to determine if the product was indeed III. Following the procedure previously described[6] a product was obtained which was identical in all respects with the product we obtained from pulegone, namely a mixture of *cis*- and *trans*-2-acetoxypulegone. In addition, the recovered unchanged starting material was found by gas chromatography to be approximately 80% pulegone and 20% isopulegone.

## Experimental

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-5 spectrophotometer; n.m.r. spectra were determined with the Varian A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane as an internal standard (δ = 0). Gas chromatograms, except where noted, were obtained with the Aerograph Hy-Fi gas chromatograph using a hydrogen flame detector and a column $^1/_8$ in. by 5 ft. of 5% SE-30 on acid-washed Chromosorb W, with hydrogen and nitrogen flow rates of 30 ml. per min.

**2-Acetoxypulegone.**—(+)-Pulegone was obtained by fractional distillation of oil of pennyroyal, and converted to 2-acetoxypulegone as described by Reitsema.[7b] The 2-acetoxypulegone used in the pyrolysis experiment had the following properties: b.p. 110–112° at 1.4 mm. (reported[7] 102° at 4 mm.); $[\alpha]^{25}\text{D}$ −14.46° ($c$ 2.31 in ethanol) (reported[7] $[\alpha]^{25}\text{D}$ −15.88°); $\lambda_{\max}^{\text{EtOH}}$ 252 mμ, ε 6214 (reported[7] $\lambda_{\max}^{\text{alc}}$ 252 mμ, ε 6010). Gas chromatography at 170° showed two components in approximately equal amounts with retention times of 5 and 5.3 min.

**Pyrolysis of 2-Acetoxypulegone.**—A solution of 4.85 g. of 2-acetoxypulegone in 25 ml. of benzene was slowly passed through a 1.5 cm. × 17 cm. Pyrex column packed with $^3/_{32}$-in. glass helices, at 450°; the solution was forced through the column under positive nitrogen pressure. The gas chromatogram, using a thermistor detector, of the benzene eluent showed two components in the ratio of 0.33 to 0.67. The component in smaller amount was very similar in retention time to 3-methylcyclohexanone, and may be 3-methyl-2-cyclohexenone, which could arise by the formation of piperitenone followed by retroaldolization during the course of the pyrolysis. This product was shown not be be thymol by gas chromatographic comparison with an authentic sample. The component of longer retention time and in larger amount was found to be menthofuran. Removal of the benzene at reduced pressure also resulted in the removal of the compound of lower molecular weight, and gas chromatographic analysis showed only the presence of menthofuran with minor impurities (less than 5%). The benzene eluent was found to contain 1.5 g. of menthofuran (43% yield) and no unchanged 2-acetoxypulegone. Charred products remaining on the pyrolysis column presumably accounted for the remainder of the starting material. When the pyrolysis was conducted at temperatures lower than 450° unchanged 2-acetoxypulegone was found to be present according to the gas chromatogram.

The menthofuran had the following properties after distillation: $\lambda_{\max}^{\text{EtOH}}$ 220 mμ, ε 5852; $[\alpha]^{25}\text{D}$ +87.46° ($c$ 1.87 in ethanol) (reported $[\alpha]^{25}\text{D}$ +81°[10a] for natural menthofuran, and $[\alpha]\text{D}$ +92 for menthofuran prepared from pulegenol sulfonic ester); the infrared spectrum was identical in all respects with that previously recorded[11]; the n.m.r. spectrum showed the methyl group on the cyclohexane ring as a doublet ($J$ = 5.5 c.p.s.) centered at δ 1.07, the methyl on the furan ring as a doublet ($J$ = 1 c.p.s.) centered at δ 1.85, and the aromatic hydrogen on the furan ring at δ 6.84. The autoxidation product (m.p. 186–187°) and maleic anhydride adduct (m.p. 132–133°) of the isolated menthofuran were identical in melting points to those previously reported.[10a,b]

**2-Acetoxypulegone from Isopulegone.**—(−)-Isopulegone was pared from isopulegol acetate as follows: a solution of 15.5 g. of isopulegol acetate, 2.4 g. sodium, and 30 ml. of 95% ethanol was refluxed for 4 hr. After cooling, the solution was adjusted to pH 6 with dilute sulfuric acid, and then extracted with ether. The ether extract, after washing with water and drying over anhydrous magnesium sulfate, gave on distillation 8.9 g. (73%) of isopulegol, b.p. 40–41° at 0.1 mm.; $\nu_{\max}^{\text{film}}$ 3450, 1643, 890 cm.$^{-1}$.

A solution of 8.6 g. of isopulegol in 50 ml. dry acetone was cooled in an ice bath and treated with Jones' reagent[12] until the brown color persisted. Water was added and the solution extracted with ether. After washing with water and drying over anhydrous magnesium sulfate, the extract was distilled to give 5.1 g. (60%) of isopulegone, b.p. 52–54° at 0.7 mm.; $\nu_{\max}^{\text{film}}$ 1710, 1643, 891 cm.$^{-1}$; $[\alpha]^{25}\text{D}$ +4.33° ($c$ 2.50 in ethanol). This optical rotation indicates the presence of 11% (+)-iso-isopulegone, $[\alpha]\text{D}$ +144.4°, and 89% (−)-isopulegone, $[\alpha]\text{D}$ −13.5°.[13] The infrared spectrum and gas chromatogram of this product indicated the absence of any pulegone.

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(9) We wish to thank the referee for suggesting such a mechanism.

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(11) Y. R. Naves, *Compt. rend.*, **237**, 704 (1953); *Soc. chim. France*, **1954**, 657.

(12) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, **1953**, 2555.

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The prepared isopulegone was treated with mercuric acetate as previously described. The acetoxy ketone fraction obtained in 25% yield was found to be identical in infrared and n.m.r. spectra, and in its gas chromatogram with the product obtained from (+)-pulegone. The gas chromatogram of the residue showed only the presence of 80% pulegone and 20% isopulegone.

## Reductions with Triphenyltin Hydride

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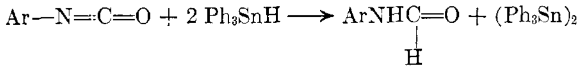
*Received November 2, 1962*

As part of a continuing study on the scope of hydrogenolyses with triphenyltin hydride we are reporting on the reactions of organo-isocyanates, isothiocyanates, and Schiff bases with triphenyltin hydride.

When phenyl isocyanate or α-naphthyl isocyanate was treated with two equivalents of triphenyltin hydride, the corresponding arylformamides were produced in 40–50% yield. This is distinctly different



$$\mathrm{Ar{-}N{=}C{=}O} + 2\,\mathrm{Ph_3SnH} \longrightarrow \mathrm{ArNH}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{C}}\mathrm{{=}O} + (\mathrm{Ph_3Sn})_2$$

Ar=Ph, α-Naphthyl

from the reaction of isocyanates with lithium aluminum hydride[4] which produces the corresponding N-methylamines. Another advantage of this reaction is that no hydrolysis step is required as in the case of lithium aluminum hydride reactions.

The reaction of phenyl isothiocyanate with triphenyltin hydride takes a different course. From this reaction mixture, hexaphenylditin, and bis-(triphenyltin) sulfide were isolated and identified by mixture melting points with known samples. This indicates that the carbon–sulfur bond is more labile than the carbon–oxygen bond to hydrogenolysis by triphenyltin hydride. In addition to the above products a basic liquid mixture which had a strong odor of an isocyanide was obtained. Infrared spectra indicated the presence of an aryl isocyanide and aromatic amines. Diazotization of the distilled reaction products and treatment with β-naphthol gave an orange product indicating the presence of a primary aromatic amine. Strong, but not completely conclusive, evidence for the identification of the products were the vapor phase chromatographs, using two different columns and three different temperatures, which showed three bands whose retention times in all cases matched those of known samples of aniline, N-methylaniline and phenyl isocyanide.

These reductions of the isothiocyanates by triphenyltin hydride may be contrasted with the reduction with lithium aluminum hydride which reacts with aryl isothiocyanates to give the corresponding N-methylamines.[5]

Since the presence of aniline in the reaction of triphenyltin hydride with phenyl isothiocyanate suggested the presence of a Schiff base as a possible intermediate, benzalaniline was treated with triphenyltin hydride. The product N-phenylbenzylamine was isolated in 35% yield. The low yield of the amine is probably due to decomposition of the hydride by the amine formed. This amine decomposition has been noted by a number of workers.[6] The other product of the reaction was hexaphenylditin, which was identified by mixture melting point with a known sample.

### Experimental

**α-Naphthyl Isocyanate with Triphenyltin Hydride.**—α-Naphthyl isocyanate (3.38 g., 0.02 mole) was added to 14 g. (0.040 mole) of triphenyltin hydride and heated at 80° for 1 hr. Extraction of the cooled, completely solidified, reaction mixture with hot chloroform followed by filtration and cooling afforded a white solid, m.p. 210–220°. An additional crop, m.p. 200–210°, was obtained from the mother liquor. The chloroform was finally removed under vacuum leaving a yellow-white solid, melting at 118–124°. This solid was washed with ethanol leaving behind a white solid, m.p. 220–225°. The ethanol solution was concentrated depositing a white solid, m.p. 190–200°. Water was added to the hot ethanol solution until cloudy, and on cooling a needle-like crystalline product was obtained, m.p. 116–128°. This product was dissolved in hot ethanol (charcoal), and cooled to give a white product, m.p. 123–126°. Recrystallization from benzene–heptane gave 1.43 g. (41%) of colorless α-naphthylformamide, m.p. 137.8–138.5°, whose infrared spectrum was superimposable upon that of known α-naphthylformamide. A mixture melting point with authentic α-naphthylformamide showed no depression (1:1 mixture, m.p. 137.8–138.8°).

The combined solids melting around 200° were recrystallized four times from benzene–heptane to give hexaphenylditin, m.p. 228–231°. A mixture melting point with known hexaphenylditin showed no depression.

**Phenyl Isocyanate with Triphenyltin Hydride.**—A mixture of 2.4 g. (0.02 mole) of phenyl isocyanate and 15 g. (0.043 mole) of triphenyltin hydride was heated at 100° for 4 hr. On cooling, the reaction mixture solidified. It was extracted overnight with water in a Soxhlet extractor. Distillation of the water *in vacuo* gave a yellow oil, which was recrystallized from ether–pentane to give a product, m.p. 45.4–47.0°. Recrystallization from ether-pentane (charcoal) did not alter the melting point, 1.35 g. (55%). The infrared spectrum was superimposable upon that of known N-phenylformamide and admixture melting point with a known sample of N-phenylformamide showed no depression (1:1 mixture, m.p. 45.6–47.1°).

The hexaphenylditin left after extraction was recrystallized from benzene–heptane to give a product, m.p. 230–231°, showing no depression upon admixture with a known sample of hexaphenylditin.

**Phenyl Isothiocyanate with Triphenyltin Hydride.**—A mixture of 2.8 g. (0.02 mole) of phenyl isothiocyanate and 28 g. (0.080 mole) of triphenyltin hydride was heated at 90° for 3 hr. Upon cooling, the reaction mixture solidified. It was then heated to 170° under vacuum and the vapors were collected in a flask in a Dry Ice–acetone bath. Vapor phase chromatography of the liquid product, which smelled strongly of an isocyanide, showed three bands which were identified as aniline, N-methylaniline and phenyl isocyanide by comparison with the vapor phase chromatographic behavior of known standards, using two different columns [K-polyethylene glycol (Carbowax 1500), R-polyglycol (Ucon LB-550-X)] and three different temperatures (179°, 189°, 194°) for comparison. The infrared spectrum showed the presence of aromatic amines and an aromatic isocyanide [NH stretch 3450 cm.$^{-1}$ and 3400 cm.$^{-1}$ (shoulder), C—N 1345 cm.$^{-1}$ (primary amine) and 1265 cm.$^{-1}$ (secondary amine), R—N=C 2145 cm.$^{-1}$]. Diazotization of the distilled reaction products and treatment with α-naphthol gave rise to an orange product indicating the presence of a primary aromatic amine.

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[2] To whom inquiries should be sent.

[3] Sponsored by the U. S. Army Research Office (Durham), whose support we are happy to acknowledge.

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