

washed with water, dried (Na_2SO_4), and evaporated at reduced pressure to give 1.40 g of the azide **4**, thick oil, ir (liquid film) 2130 cm^{-1} (azide).

The azide was warmed for 2 hr at 70° in 10 ml of anhydrous benzyl alcohol. The mixture was diluted with ethyl ether and extracted with 2 *N* sodium carbonate. The cooled alkaline solution was acidified with 2 *N* hydrochloric acid to pH 4 and reextracted with ether which was washed with water and dried (Na_2SO_4); solvent was evaporated off at reduced pressure. The oily residue was crystallized from ethanol-water to give 500 mg (28%) of *cis*- N,N' -dicarbobenzyloxy-5-amino-DL-proline, mp $141\text{--}142^\circ$.

Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_6$: C, 63.31; H, 5.57; N, 7.03. Found: C, 63.39; H, 5.65; N, 7.06.

Registry No.—**1**, 24377-91-1; **2**, 24377-92-2; **3**, 24377-93-3; **5**, 24377-94-4; α -keto- δ -acetylaminovaleric acid (2,4-dinitrophenylhydrazone), 24378-14-1.

A Facile Preparation of 3-Thujene from Thujone

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The bicyclic monoterpene 3-thujene (**1**) is much less readily available from natural sources than is thujone (**2**). The methods previously used^{1,2} for obtaining **1** from **2** involve reduction to the thujyl alcohols, separation of isomers, and eliminations. We have found that it is possible to obtain **1** from **2** in a rather simple procedure which is applicable to large-scale work by use of the Bamford-Stevens rearrangement.³

Thujone (**2**) was readily converted to the *p*-toluenesulfonylhydrazone which was initially decomposed with a solution of sodium in ethylene glycol. The hydrocarbon product was analyzed by preparative vpc and shown to contain 3-thujene (**1**, 42%), 2-thujene (**3**, 16%), γ -terpinene (**4**, 13%), a fourth unidentified compound, and a trace of *p*-cymene. Using acetamide as a solvent,⁴ the hydrocarbon product (97% yield) consisted of **1** (80%) and **4** (20%), **4** being slightly contaminated with an unidentified isomer. 3-Thujene was characterized by its spectral properties and by conversion to terpinene dihydrochloride.⁵ This procedure therefore represents a simple process for obtaining 3-thujene from readily available thujone.

Experimental Section⁶

***p*-Toluenesulfonylhydrazone.**⁷—Hydrazine hydrate (40 g, 85%) was slowly added to a benzene solution of 60 g of *p*-toluene-

sulfonyl chloride (recrystallized from an ether-ligroin mixture) at 5° through the condenser into a 500-ml flask. After 2 hr the solid was filtered and recrystallized from hot water. The yield was 42.6 g (72%), mp $110\text{--}112^\circ$ (lit.⁷ 112°).

Thujone *p*-Toluenesulfonylhydrazone.—*p*-Toluenesulfonylhydrazone (42.6 g) and 40 g of **2**, $[\alpha]_D^{20} +20.13^\circ$, were dissolved in 200 ml of ethanol and refluxed in a 500-ml flask for 3.5 hr until the reaction was complete as indicated by thin layer chromatography. Following reflux, the ethanol was removed under reduced pressure until a precipitate formed, and then the mixture was heated on a steam bath to effect solution. The solution was cooled to effect crystallization; the crystals were filtered, recrystallized from ethanol, and dried. The yield was 25.6 g (35%), mp $126\text{--}129^\circ$, $[\alpha]_D^{20} +105.7^\circ$; ir (CHCl_3) 3310 (NH), 2980, 1610, 1170 cm^{-1} .

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{SO}_2$: C, 63.75; H, 7.50; N, 8.75. Found: C, 63.99; H, 7.74; N, 8.63.

3-Thujene (1). I. **Ethylene Glycol as Solvent.**—The hydrazone (**5** g) and 50 ml of 1.5 *N* sodium in ethylene glycol were placed in a 100-ml flask. Most of the solid dissolved immediately and the remainder dissolved on the application of heat. Nitrogen evolution continued steadily for 15 min and the resulting organic layer was then distilled off at $141\text{--}175^\circ$ yielding 1.5 ml of product. The vpc analysis indicated four products: 3-thujene (**1**, 42%), 2-thujene (**3**, 16%), contaminated slightly with another compound γ -terpinene (**4**, 13%), and 20% of an unidentified mixture.

II. **Acetamide as Solvent.**—The acetamide (200 g) was melted in a 500-ml three-necked flask and purged with oxygen-free nitrogen. The acetamide was cooled to 100° and 6.0 g of sodium was added in small quantities under a nitrogen atmosphere (extreme care must be taken to avoid combustion). The hydrazone (**38.6** g) was added and the temperature held at $140\text{--}150^\circ$. Nitrogen evolution ceased after 25 min and the reaction mixture was cooled slightly. Water (200 ml) was added and the organic layer was extracted into petroleum ether. The ethereal solution was dried (MgSO_4), filtered, concentrated, and distilled giving 15.9 g (97%) of mixed hydrocarbon product. The mixture was readily separated *via* preparative vpc and **1** was characterized as follows: n_D^{20} 1.4471, $[\alpha]_D^{20} -32.05^\circ$, bp $150\text{--}151^\circ$; ir (neat) 2985, 2881, 3057 cm^{-1} ; nmr (neat) δ 0.02 (t, 1, $J = 3\text{ Hz}$), 0.90 (m, 2), 0.98 (d, 6, $J = 3\text{ Hz}$), 1.35 (m, 1), 1.76 (q, 3, $J = 2\text{ Hz}$), 2.30 (m, 2), 4.90 (m, 1); mass spectrum (70 eV) m/e 136, 93 (lit.⁸).

Terpinene Dihydrochloride.⁵—To 5 ml of glacial acetic acid was added 0.20 g of **1** and the solution was saturated with gaseous HCl. The mixture developed a red color after 9 hr of standing and was then poured over ice. The resulting solid was filtered and recrystallized from methanol: mp $47\text{--}49^\circ$; nmr (CDCl_3) δ 1.68 (s, 3), 1.90 (d, 6, $J = 6\text{ Hz}$), 1.98 (s, 9).

The absolute configurations of 3-thujene (**1**), thujone (**2**), and 2-thujene (**3**) are those verified by Norin.^{9,10}

Registry No.—**1**, 3917-48-4; **2**, 546-80-5; **2 p**-toluenesulfonylhydrazone, 18791-12-3.

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Alkaline Cleavage of Phosphetane Oxides

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Recently, we reported the alkaline cleavage of several heterocyclic phosphine oxides.¹ In all but one

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