o-Aminophenol, in benzene at room temperature, gave rise to the azine **3**, which on subsequent reduction produced *o*-benzoquinone mono(*o*-acetoxy phenylhydrazone) (**4**).

It is interesting to point out that the oxidation of benzil dihydrazone (**5**) treated with silver(II) oxide produced diphenylacetylene in 95% yield, a better yield than that obtained by oxidation with HgO (81%).[8]

The results of oxidation involving a wide range of functional groups are summarized in Table II.

Experimental Section

The general method employed for the reactions was to dissolve the substance to be oxidized (1–5 mmol) in a suitable solvent. Then the silver(II) oxide, prepared according to Hammer and Kleinberg,[1] was added and the mixture was allowed to stand at room temperature with stirring and sampling at frequent intervals for tlc analysis of the extent of the reaction. If the chromatoplate spot corresponding to the starting material remained after several hours, the mixture was heated to the boiling point of the solvent. When the starting material had been used up, the reaction was stopped by filtering the silver or Ag_2O formed in the reaction. The purification of the products was carried out by chromatography either on alumina or on silica gel. The yields given are those of the pure products that were identified by melting point, uv, ir, nmr, and mass spectra and compared with authentic samples or spectra described in some detail.

2,6,2′,6′-Tetramethylazolenzene.—A solution of 1 g of silver(II) oxide was allowed to reflux for 5 hr. The solution was filtered and chromatographed on alumina, Alcoa F-20 (150 g). From the fractions eluted with benzene, 320 mg (33%) of orange-red crystals, mp 50°, was obtained: λ_{max} 213 nm (ϵ 26,400), 243 (10,100), 248 (11,600), 254 (12,300), 260 (10,250), 300 (8850), and 455 (840); ir 1585 cm^{-1}; nmr δ 2.4 (singlet) (TMS = 0) (12 protons of methyl on aromatic ring) and 7.1 ppm (singlet) (six protons, aromatic). *Anal.* Calcd for $C_{16}H_{16}N_2$: C, 80.63; H, 7.61; N, 11.76; mol wt, 238.32. Found: C, 80.49; H, 7.41; N, 11.52; mol wt, 238 (mass spectrum).

o-Benzoquinone Azine 3.—A mixture of 6 g of *o*-aminophenol and 21 g of silver(II) oxide in 200 ml of benzene was stirred at room temperature for 2 hr. After filtering, 2.8 g (45%) of crystals were obtained: mp 245°; λ_{max} 235 nm (ϵ 30,400) and 430 (28,700); ir 3370 and 1575 cm^{-1}. *Anal.* Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; O, 15.08; N, 13.20; mol wt, 212.2. Found: C, 67.46; H, 3.80; O, 15.17; N, 12.74; mol wt, 212 (mass spectrum).

***o*-Benzoquinone Mono(*o*-acetoxy)phenylhydrazone** (**4**).—A mixture of 200 mg of *o*-benzoquinone azine (**3**), 10 ml of acetic acid, 10 ml of acetic anhydride, and 2 g of zinc dust was heated for 2 hr at the steam bath, filtered, and poured into ice. The solid formed was crystallized from methanol: yield 152 mg (63%); mp 279–280°; λ_{max} 240 nm (ϵ 17,200) and 396 (24,000); ir 3270, 1700, and 1605 cm^{-1}. *Anal.* Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93; O, 18.73; mol wt, 256.25. Found: C, 65.78; H, 4.34; N, 10.81; O, 18.93; mol wt, 256 (mass spectrum).

Diphenylacetylene.—To 240 mg of benzildihydrazone, obtained by the method of Cope, Smith, and Cotter,[8] in 50 ml of benzene, 500 mg of silver(II) oxide was added and the mixture was stirred for 2 hr. After filtering, the solvent was evaporated and the residue was sublimed at 60° (0.5 mm); the yield was 170 mg (95%), mp 58°. *Anal.* Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66; mol wt, 178.22. Found: C, 94.09; H, 5.74; mol wt, 178 (mass spectrum).

Registry No.—**1**, 554-55-2; **3**, 34562-05-5; **4**, 34562-06-6; diphenylacetylene, 501-65-5; AgO, 1301-96-8.

Acknowledgments.—We thank the Consejo Nacional de Ciencia y Tecnología de México for financial help in the publication of this work, and Dr. Harold Kwart for aid in the preparation of the manuscript.

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The Hydrochlorination of Thujopsene

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In recent years much work has been done on the chemistry of the cyclopropylcarbinyl cation system.[1] The naturally occurring sesquiterpene (−)-thujopsene (**1**) contains a conjugated cyclopropyl olefin functionality which is readily protonated to form the rearrangement-prone cyclopropylcarbinyl cation system. Most of the isomerization studies on this interesting molecule have been performed in aqueous media with oxygen-containing acids.[2–8] We recently reported[9] the results of our study on the isomerization products obtained under nonaqueous conditions employing oxygen-containing acids. Friedrich[10] has also shown that the major product obtained upon treatment of (−)-thujopsene in refluxing 12 *M* HCl in dioxane is the bicyclic neopentyl chloride **5**. We have subsequently investigated the action of anhydrous hydrogen chloride on (−)-thujopsene and report our results below.

Treatment of **1** with anhydrous hydrogen chloride at 5° led to a rapid absorption of the gas. The initial crystalline product, although stable for days at −20° either as a solid or in a nonprotic solvent, rearranged upon warming to room temperature to other isomeric products. The formation of these products was easily followed by nmr spectroscopy and the pertinent spectral data are summarized in Table I. From this data the structures of the various intermediates were assigned.

The initial crystalline hydrochlorination product exhibited four methyl singlets and no vinyl hydrogen absorption in the nmr spectrum at −10°, and clearly was expected simple 1,2-addition product, tertiary chloride **2**. The stereochemistry of the chlorine atom is assigned by approach from the less hindered α face, as has been found in the stereochemistry of hydroboration and epoxidation of (−)-thujopsene.[11]

Subsequent warming of the deuteriochloroform solution to 20° showed the gradual disappearance of resonance peaks due to **2** and the concomitant appearance of new peaks, notably the transformation of one of the original methyl singlets into a vinyl methyl and the appearance of a vinyl hydrogen singlet at δ 5.05 and a two-proton singlet at δ 3.59 of an isolated chloromethyl grouping. This data is consistent with structure **3**, the 1,4-addition product of hydrogen chloride to thujopsene.

Further warming or standing at 20° for a longer time afforded a new set of resonance peaks containing a well-

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TABLE I

NMR CHEMICAL SHIFTS FOR THE THUJOPSENE HYDROCHLORIDES[a]

2	3	4	Widdrol (6)[b]	5
0.55 (s, 3)	1.00 (s, 3)	1.08 (s, 6)	1.08 (s, 6)	1.05 (s, 6)
1.00 (s, 3)	1.04 (s, 3)	1.22 (s, 3)	1.22 (s, 6)	1.08 (s, 3)
1.12 (s, 3)	1.08 (s, 3)	1.59 (s, 3)		1.17 (s, 3)
1.81 (s, 3)	1.70 (s, 3)	2.27 (d, d, 1, J = 14, 9 Hz)	1.94	3.31 (s, 2)
	3.59 (s, 2)	2.95 (d, d, 1, J = 14, 6 Hz)	2.48	5.11 (s, 1)
	5.05 (s, 1)	5.48 (d, d, 1, J = 9, 6 Hz)	5.48	

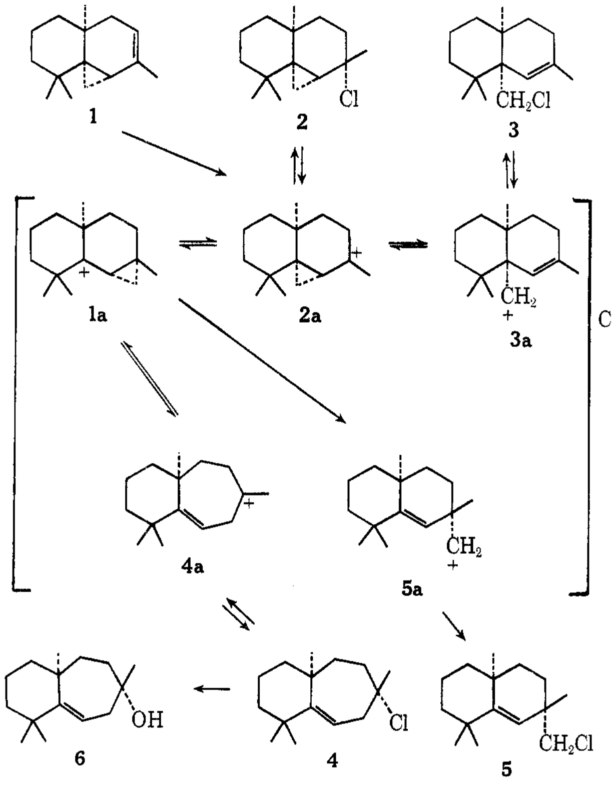
[a] Expressed as δ values from TMS in $CDCl_3$. [b] Coupling constants for the last three entries are identical with those shown for compound 4.

defined doublet of doublets at δ 5.48 coupled with upfield nonequivalent allylic protons at δ 2.95 and 2.27 as the resonances for compound **3** vanished. Bicyclic structure **4** is assigned to this new compound by the close similarity of its nmr spectrum with that of the known[12] tertiary alcohol widdrol (see Table I), and by the fact that widdrol can be isolated when this intermediate is treated with refluxing aqueous sodium carbonate.

The final thermodynamic product obtained upon warming to 40° afforded an nmr spectrum identical in all respects with that of the neopentyl chloride **5** previously reported by Friedrich[10] as the major product obtained by treatment of thujopsene with 12 M HCl in refluxing dioxane.

The formation of these products is readily rationalized *via* the cyclopropylcarbinyl cation intermediates outlined in Scheme I. Protonation of (−)-thujopsene to cation **2a** and chloride ion capture leads directly to the crystalline 1,2-addition product **2**. Subsequent thermal ion pair decomposition then affords cation **3a**, which generates the 1,4-addition product **3**. Further rearrangement to cation **4a** has been previously well documented by Dauben and Friedrich[4] and the capture of chloride ion by this cation to give tertiary chloride **4** should afford the same stereochemistry as that of widdrol (**6**) itself, formed under acid hydration conditions.[4] Final thermal ion pair decomposition *via* homoallylic cation **5a** then leads to the most stable neopentyl chloride **5**, as has been reported previously by Friedrich[10] *via* the same mechanistic rationale.

SCHEME I



Earlier studies[13−15] have shown that such rearrangements are quite general for cyclopropylcarbinyl systems. Our present observations on the formation of intermediate chlorides in the hydrochlorination reaction lends additional support to the finite existence of homoallylic cations such as **3a**, **4a**, and **5a**. No chloride product consistent with the capture of cation **1a** was detected by nmr, a result not too surprising since this tertiary ring fusion cation should be quite sterically hindered to capture by an external nucleophile.

Neopentyl chloride **5** is completely stable to the action of refluxing 10% aqueous sodium carbonate, whereas similar treatment of crystalline chloride **2** afforded a mixture of thujopsene (**1**) and widdrol (**6**) in a 2:1 ratio. The same ratio was also obtained upon the identical treatment of a 50:50 mixture (by nmr) of chlorides **3** and **4** which contained less than 5% of **2**. These results imply the rapid interconversion of ion pairs **2a**, **3a**, and **4a** to afford the same product ratio irrespective of starting material under these mildly basic conditions.

A recent report[16] that treatment of (−)-thujopsene (**1**) with anhydrous hydrogen bromide at 0° leads to the neopentyl bromide analog of **5** has been confirmed by us. No crystalline 1,2-addition tertiary bromide product could be obtained under these conditions, undoubtedly due to the higher reactivity of such a molecule as compared with the corresponding chloro compound **2**.

Experimental Section

Materials and Equipment.—(−)-Thujopsene was readily obtained in 99% purity by careful fractional distillation of Hibawood oil through a 2-ft Goodloe column, bp 67–68° (0.5 mm), $n^{20}D$ 1.5050, $[\alpha]^{25}D$ −92.5° (neat).

Spectra were recorded using a Perkin-Elmer 457 grating ir spectrophotometer and a Varian A-60A nmr spectrometer. Com-

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2α-Chloro-1α,9α-methano-2β,8,8,10α-tetramethyldecalin (2).—(−)-Thujopsene (102 g, 0.5 mol) was cooled to 5° and vigorously agitated while anhydrous hydrogen chloride was passed in over 1.7 hr. Gas absorption ceased when 1 molar equiv had been added and the reaction mixture crystallized with an attendant temperature rise to 25°. Ice-cold hexane (100 ml) was added and the mixture was rapidly filtered through a cold sintered glass funnel to afford 63 g of solid material, mp 40–43° dec. A sample recrystallized from hexane at −50° exhibited mp 42–45° dec: ir (CCl_4, 0°) 1255, 1160, 1150, 1030, 1000, 827 cm^{-1}; nmr ($CDCl_3$, −10°) δ 0.55, 1.00, 1.12, 1.81 (s, 3 each); $[\alpha]^0D$ −95° (*c* 20%, $CHCl_3$).

A crystalline sample stored under nitrogen at −20° for 10 days showed little signs of decomposition.

Anal. Calcd for $C_{15}H_{25}Cl$: C, 74.81; H, 10.46; Cl, 14.72. Found: C, 74.91; H, 10.48; Cl, 14.53.

9α-Chloromethyl-2,8,8,10α-tetramethyl-1-octalin (3).—The nmr sample (at −10°) of tertiary chloride **2** was warmed to 20° for 0.4 hr and the spectra were recorded. The major component showed the following nmr resonances: δ 1.00, 1.04, 1.08 (s, 3 each), 1.70 (s, 3, vinyl CH_3), 3.59 (s, 2), 5.05 (s, 1, $W_{h/2}$ = 4 Hz); ir (CCl_4) 1080, 845, 648 cm^{-1}.

4α-Chloro-4β,7α,11,11-tetramethylbicyclo[5.4.0]undec-1-ene (4).—The above nmr sample was warmed to 40° for an additional 1.0 hr and the spectra were recorded. The major component showed the following nmr resonances: 1.08 (s, 6), 1.22, 1.59 (s, 3 each), 2.27 (d, d, 1, J = 14, 9 Hz), 2.95 (d, d, 1, J = 14, 6 Hz), 5.48 (d, d, 1, J = 9, 6 Hz); ir (CCl_4) 1230, 672 cm^{-1}.

2α-Chloromethyl-2β,8,8,10α-tetramethyl-1(9)-octalin (5).—Continued warming of the above nmr sample at 40° for an additional 20 hr gave the stable neopentyl chloride **5** with the following nmr resonances: δ 1.05 (s, 6), 1.08, 1.17 (s, 3 each), 3.31 (s, 2), 5.11 (s, 1, $W_{h/2}$ = 2.5 Hz); ir (CCl_4) 1020, 925, 860, 718, 662 cm^{-1}; $[\alpha]^{25}D$ +75° (*c* 20%, $CDCl_3$). These data are identical with those reported by Friedrich[10] for chloride **5**.

Treatment of neopentyl chloride **5** at reflux for 6 hr with 10% aqueous sodium carbonate gave recovered unchanged starting material.

4β,7α,11,11-Tetramethylbicyclo[5.4.0]undec-1-en-4α-ol (Widdrol) (6).—An 18-g sample of crystalline chloride **2** was heated to 60° for 2.0 hr. The nmr spectrum showed that the products at this point were approximately an equimolar mixture of chlorides **3** and **4** with only trace amounts of chlorides **2** and **5**. Water (150 ml) and sodium carbonate (10 g) were added and the mixture was allowed to reflux for 6 hr. The mixture was cooled and the organic layer was separated. Analysis by gas chromatography showed three peaks identified as thujopsene (**1**, 57%), an unidentified hydrocarbon (18%), and widdrol (**6**, 25%). Distillation on a micro-still head afforded 12.2 g of liquid fractions, bp 100–110° (1.5 mm), with an infrared spectrum virtually identical with that of thujopsene (**1**). The fractions boiling at 125–135° (1.5 mm) (4.0 g) crystallized and were recrystallized from methanol to afford widdrol (**6**): mp 89–90°; nmr ($CDCl_3$) δ 1.08, 1.22 (s, 6 each), 1.94 (d, d, 1, J = 14, 9 Hz), 2.48 (d, d, 1, J = 14, 6 Hz), 5.48 (d, d, 1, J = 9, 6 Hz). The infrared spectrum was identical with that reported by Enzell[12] for widdrol.

The same products were also obtained in a similar ratio when the crystalline hydrochloride **2** was treated directly with 10% aqueous sodium carbonate at reflux for 3 hr.

Treatment of Thujopsene with Anhydrous Hydrogen Bromide.—(−)-Thujopsene (51 g, 0.25 mol) was cooled to 0° and vigorously agitated while anhydrous hydrogen bromide was passed in. Absorption was slow and the theoretical amount was consumed in 4.5 hr. The dark colored mixture did not crystallize as had been the case for the chloride analog. Hexane (50 ml) was added and the mixture was washed neutral with cold 10% aqueous sodium carbonate solution. The solvent was removed at reduced pressure and distilled, affording 51.5 g of yellow oil: bp 125–128° (1.0 mm); $n^{20}D$ 1.5170; $\alpha^{25}D$ +68° (neat); ir (neat) 1630, 1250, 1230, 1021, 985, 925, 868, 668, 650 cm^{-1}; nmr ($CDCl_3$) δ 1.06 (s, 6), 1.08, 1.17 (s, 3 each), 3.25 (s, 2), 5.10 (s, 1). The spectral data are identical with those reported by Itô[16] and coworkers for the bromide analog of chloride **5**.

Registry No.—**1**, 470-40-6; **2**, 34905-90-3; **3**, 34905-91-4; **4**, 34905-92-5; **5**, 32540-35-5; **5** bromide analog, 34905-94-7; **6**, 6892-80-4.

Aniline Derivatives of Tetrakis(hydroxymethyl)phosphonium Chloride

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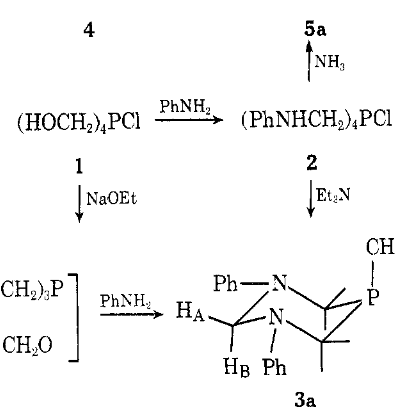
The development of flame-retardant finishes for cotton based on the reaction of tetrakis(hydroxymethyl)phosphonium chloride (**1**) with polyfunctional amines such as melamine[2] has led to the investigation of many other nitrogen compounds as resin-forming substrates.[3,4] Secondary amines give well-defined monomeric products,[5,6] but primary amines, such as cetylamine,[7–9] have thus far given only polymeric products.[7–12] In this paper we report our investigation of the reaction of **1** and some of its derivatives with aniline, which led to a series of well-defined crystalline compounds.

Aniline reacts readily with **1** in ethanol or acetone at room temperature, displacing all four hydroxyl groups (Scheme I).[13] The product, tetrakis(anilino-

Scheme I



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