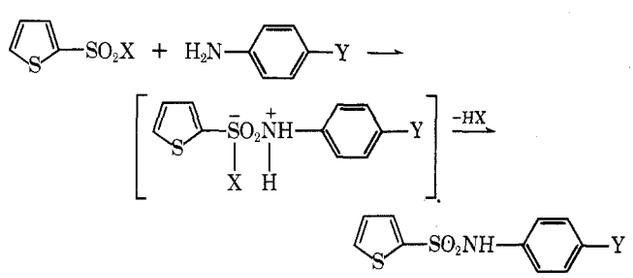
value for the entering nucleophiles, obtained for the reactions of 2-thiophenesulfonyl chloride with some meta- and para-substituted anilines,[1] is +0.79. The comparison between the β values suggests a greater degree of S–N bond formation in the transition state with respect to S–Hal bond breaking. This finding implies the formation of an intermediate complex along the reaction path. Nevertheless the Brϕnsted coefficients must be regarded, as a simple mechanism criterion, with great caution owing to the nonhomogeneous comparison between log k_2 and pK_a,[9] since the rate constants were measured in methanol solution, while the pK_a values for anilines and hydrogen halides were determined in aqueous solution. The pK_a values reported for hydrogen halides, besides, are rather uncertain.[10]

A further interesting result is that the rates and the activation parameters for 2-thiophenesulfonyl fluoride reactions are almost equal with aniline and *p*-anisidine; this suggests that the rate-determining step is the S–F bond breaking in the transition state.

For the reactions of 2-thiophenesulfonyl chloride and bromide, instead, the rate-determining step is the nucleophilic attack to the sulfonyl halide. In fact the reaction rates (Table I) and the activation energies (Table II) are affected by the basicity of the nucleophilic reagent and not by the leaving halogen nature.

In conclusion the data on the reactivities of 2-thiophenesulfonyl halides and the relative activation parameters could fit well with a two-step addition–elimination mechanism S_AN, the rate-determining step being the S–N bond formation for 2-thiophenesulfonyl chloride and bromide and the S–F bond breaking for sulfonyl fluoride (see Scheme I).

Scheme I



Experimental Section

Materials. 2-Thiophenesulfonyl chloride was obtained by adding at 20°, under stirring, 33.6 g (0.4 mol) of thiophene to a mixture containing 66 ml (1 mol) of chlorosulfonic acid and 83 g (0.4 mol) of phosphorus pentachloride, following the procedure already described,[11] 70% yield, bp 92–93° (1 mm), mp 31–32° from petroleum ether (bp 30–60°).

2-Thiophenesulfonyl Fluoride. To an aqueous solution (30 ml) containing 7.4 g (0.2 mol) of ammonium fluoride, 18.3 g (0.1 mol) of 2-thiophenesulfonyl chloride was added. The mixture was refluxed for 5 hr, then treated with warm water and extracted with ether. The evaporated extract gave the products, 90% yield, bp 75–76° (1 mm).[12]

2-Thiophenesulfonyl Bromide. This product was synthesized using the method reported for benzenesulfonyl bromide.[13]

To 10.7 g (0.06 mol) of 2-thiophenesulfonyl hydrazide (see later) in 200 ml of 10% hydrochloric acid was added at 20° an aqueous solution (35 ml) containing 2.4 g (0.02 mol) of potassium bromide and 6.7 g (0.04 mol) of potassium bromate. The precipitate was filtered quickly, washed with cold water, and dried *in vacuo*, 60% yield, mp 48–49° from petroleum ether.

Anal. Calcd for $C_4H_3BrO_2S_2$: Br, 35.19. Found: Br, 35.28.

2-Thiophenesulfonyl hydrazide was synthesized by the method reported for benzenesulfonyl hydrazide.[14]

To 12.5 g (0.25 mol) of 85% hydrazine hydrate in 30 ml of ether was added an ether solution (30 ml) containing 18.3 g (0.1 mol) of 2-thiophensulfonyl chloride. The mixture was stirred for 30 min and the precipitate was collected and washed with cold water, 60% yield, mp 68–69° from water.

Anal. Calcd for $C_4H_6N_2O_2S_2$: N, 15.72. Found: N, 15.60.

Aniline and *p*-anisidine were commercial products purified by several distillations or crystallizations.

Methanol (R. S. Carlo Erba) was used throughout; no special purification was undertaken, since several experiments showed that elaborate purification was unnecessary.

Kinetic Procedure. Rate measurements were done by a digital pH meter, Amel Model 333, equipped with a motorized burette, Amel Model 233, by continuous titration of the acid produced with 0.1 *N* sodium hydroxide, following the procedure described before.[1] The reagent concentrations ranged from *ca.* 0.0003 to *ca.* 0.013 mol for 2-thiophenesulfonyl halides and from *ca.* 0.004 to *ca.* 2 mol for the anilines, depending on the reaction rates.

The first-order rate constants were obtained from the slope of conventional plots of log $(a - x)$ against time, using the least-squares method. The activation energies were calculated from the Arrhenius equation by the least-squares method. The entropies of activation were computed for 25°, using the suitable equation.

Product Analysis. Methanol solutions of 2-thiophenesulfonyl halide (0.025 mol) and aniline or *p*-anisidine (0.15 mol) were allowed to react at room temperature until completion. Methanol was evaporated, and then the residue was treated with aqueous 40% sodium hydroxide and extracted twice with ether or filtered. The aqueous layer was acidified and the precipitate was collected, washed with water, and crystallized from aqueous ethanol: 2-thiophenesulfonanilide, mp 99–100[1]; 2-thiophene-4′-methoxysulfonanilide, mp 104°.[1]

Acknowledgments. We thank Professor A. Arcoria for helpful discussions and the Consiglio Nazionale delle Ricerche (Rome) for the financial support.

Registry No.—Thiophene, 110-02-1; chlorosulfonic acid, 7990-94-5; 2-thiophenesulfonyl hydrazide, 52260-00-1.

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Model Studies of Terpene Biosynthesis. Synthesis and Absolute Configuration of (+)-*trans*-2,2-Dimethyl-3-(2′-methylpropenyl)cyclobutanol[1]

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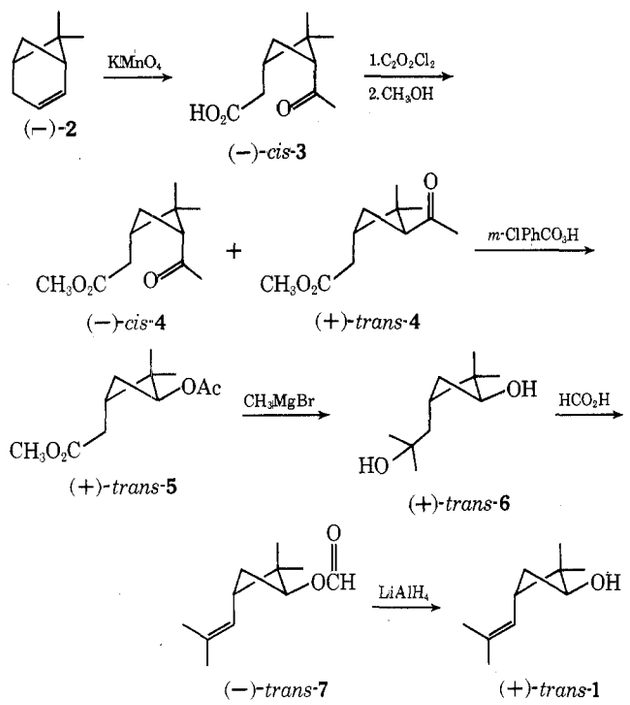
Several mechanisms have been suggested for the head-to-head rearrangement of presqualene and prephytoene

pyrophosphate to squalene and phytoene, respectively.[2] Among the proposed intermediates is a cyclobutyl species, either as a cation[2a-d,f,g] or a covalent pyrophosphate.[2e-g] In this note we describe the synthesis of a C_{10} model, (+)-*trans*-2,2-dimethyl-3-(2′-methylpropenyl)cyclobutanol (*trans*-**1**).

Scheme I



Cyclobutanol *trans*-**1** was prepared by the sequence of reactions shown in Scheme I. By choosing α-pinene (**2**) as a starting material, the cyclobutane ring and the geminal methyl groups are already assembled. Also, the cyclobutane carbon atoms which will become C_1 and C_3 in *trans*-**1** are functionalized. Of more importance, optically active α-pinene is readily available,[3] and all of the correlations necessary to establish the absolute configuration and optical purity of a key intermediate in Scheme I, pinonic acid (**3**), have been published.[4] Thus, our synthetic task involved functional group modifications and epimerization of either C_1 or C_5 in α-pinene, while retaining the configuration of the other.

Oxidation of (−)-α-pinene (**2**), 95% 1*S*,5*S*, with potassium permanganate following the procedure of Delepine[5] gave (−)-pinonic acid (*cis*-**3**) and its (−) diastereomer (*trans*-**3**). The mixture of diastereomers was evidently the result of epimerization of the very labile α-keto carbon in **3**, even though the reaction was buffered with ammonium sulfate. Although trans substitution on the ring was ultimately desired, syrupy *trans*-**3** could not be readily purified for further use in the synthetic scheme. The cis isomer, however, was easily obtained in pure form by recrystallization.

Treatment of a benzene solution of crystalline (−)-*cis*-**3** with oxalyl chloride, followed by addition of methanol, gave an equilibrium mixture of methyl pinonates which consisted of 72% (−)-*cis*-**4** and 28% (+)-*trans*-**4**. Attempted further epimerization with *p*-toluenesulfonic acid did not alter the ratio of diastereomers, while epimerization of *cis*-**4**, *vide infra*, under similar conditions resulted in the same equilibrium mixture. Esterification of the sodium salt of (−)-*cis*-**3** proceeded with less epimerization at C_3, although a small amount of the trans isomer was seen. The identities of the two diastereomers were then confirmed by glpc comparisons. The cis/trans mixture of methyl pinonates was separated by a careful spinning band distillation.

The configuration at C_3 was locked during the next step. Baeyer–Villiger oxidation of the oxo functional group in methyl pinonate was regio- and stereospecific, as expected.[6] In all cases only acetates were formed and the oxygen atom was inserted between C_3 and the carbonyl carbon with retention of configuration. Oxidation of a 72:28 cis/trans mixture of methyl pinonates gave *cis*- and *trans*-cyclobutyl acetates (**5**) in exactly the same ratio. Subsequent work indicated that separation of the cis and trans isomers, although difficult, was best accomplished before the Baeyer–Villiger reaction. When (+)-*trans*-**4** (95% trans) was treated with *m*-chloroperbenzoic acid in dichloromethane at 25°, (+)-*trans*-**5** (95% trans) was obtained. Addition of an excess of methylmagnesium iodide to (+)-**5** (95% trans) transformed the methyl ester functionality into a dimethylcarbinol and converted the cyclobutyl acetate into an alcohol. The syrupy diol was obtained in quantitative yield.

The final step required a regioselective dehydration of the tertiary hydroxyl group in diol (+)-*trans*-**6** to give the desired 2-methyl-1-propenyl group at C_3. Of the several methods tried, including treatment of the diol with iodine, the best results were obtained by heating (+)-*trans*-**6** in anhydrous formic acid. The product consisted mainly of (−)-*trans*-**7** in a ratio of about 4:1 with the methylene isomer, as well as some undehydrated mixed formates and hydroxyformates which were isolated and recycled. The cyclobutyl formate slowly decomposed in formic acid, and the progress of the reaction had to be followed carefully in order to obtain a maximum yield.

The desired product was separated from its methylene isomer and the nonolefinic products by column chromatography on 10% $AgNO_3$–silica gel. The separation was cleaner for the formate than alcohol (+)-*trans*-**1**, since the latter tended to tail on our column. The combined yield of two successive dehydrations was 42% with the proportion of *cis*-cyclobutyl alcohol in *trans*-**1** increasing from 5 to 9%. The decrease of the trans/cis ratio upon dehydration evidently is the result of a lower stability of the trans isomer to the reaction conditions. This conclusion is supported by the observation that the *cis*-diol can be dehydrated to *cis*-**7** in much better yield than the trans isomer, and the reaction mixture can be heated for extended periods without the decomposition that takes place in the trans series at longer reaction times. Also, solvolysis studies have shown that trans derivatives of **1** react more rapidly than cis derivatives.[2,7] The trans formate would presumably be less stable than *cis*-**7** in a strongly ionizing solvent such as formic acid.

Cyclobutyl alcohol (+)-*trans*-**1** (91% trans) was obtained in 86% yield from (−)-formate **7** by reduction with lithium aluminum hydride. Racemic **1** has been prepared by a different route as a 40:60 mixture with its cis isomer.[2,7] The nmr spectrum of our alcohol (91% trans) is identical with that of the isomer identified as the trans component of the 40:60 mixture.[8]

As indicated in Scheme I, the absolute configuration at C_3 in *trans*-**1**, the carbon which bears the 2-methyl-1-propenyl group, is maintained throughout the synthetic sequence, while the absolute configuration of C_1, the hydroxyl-bearing carbon, has undergone a single inversion during the epimerization which occurred during esterification of **3**. Therefore, optically active alcohol (+)-*trans*-**1** has the absolute configuration 1*S*,3*R* as shown, when prepared from (1*S*,5*S*)-α-pinene.

Experimental Section

General. Melting points (sealed capillary) and boiling points are uncorrected. Unless otherwise indicated, nmr spectra were obtained in carbon tetrachloride solution with TMS internal standard, and recorded with a Varian A-60 spectrometer. Spectra are reported in parts per million (δ) relative to TMS. Analytical gas chromatography was carried out on a Varian Model 1200 gas chromatograph with flame ionization detector, using a 500 ft × 0.03 in. open tubular column coated with Carbowax 20M. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter.

(−)-(2,2-Dimethyl-3-acetylcyclobutyl)acetic Acid, *cis*-Pinonic Acid [(−)-*cis*-3]. Oxidation of (−)-α-pinene, 95% 1*S*,5*S* (Columbia Organic Chemicals), was carried out with potassium permanganate and ammonium sulfate buffer by the procedure of Delepine.[5] The yield of crude acid varied between 40 and 60%. From the crude, mushy acid could be separated by filtration of a carbon tetrachloride solution, a small portion of insoluble racemic *cis*-pinonic acid. Addition of hexane to the filtrate then allowed crystallization of (−)-(1*R*,3*R*)-pinonic acid, which was purified by further recrystallization from carbon tetrachloride–hexane. Pure (1*R*,3*R*)-3 was obtained in about 9% overall yield: mp 69–70°, $[\alpha]^{25}D$ −93.7° (*c* 4.60, $CHCl_3$) [lit.[4a] mp 68–69°; $[\alpha]D$ +95.0° ($CHCl_3$)]; nmr ($CDCl_3$) 0.87 and 1.32 (6, s, ring methyl), 2.03 (3, s, acetylmethyl), 2.32 (2, m, H adjacent to carbonyl), 2.05 (2, m, H at C_4), and 2.89 ppm (1, t, H at C_3, $J_{2,3}$ = 8 Hz).

(−)-Methyl *cis*-(2,2-Dimethyl-3-acetylcyclobutyl)acetate, *cis*-Methyl Pinonate [(−)-*cis*-4], and (+)-Methyl *trans*-(2,2-Dimethyl-3-acetylcyclobutyl)acetate, *trans*-Methyl Pinonate [(+)-*trans*-4]. (−)-Pinonic acid, 16.0 g (0.0878 mol), was dissolved in 100 ml of benzene that had been dried over Linde 3A molecular sieves, and 8.7 ml (12.1 g, 0.101 mol) of oxalyl chloride was added. The mixture was allowed to stir at ambient temperature for 4 hr. Anhydrous methanol (100 ml) was then added and the mixture allowed to stir for an additional 1.5 hr. Solvents were removed on a rotary evaporator, the residue taken up in ether, and the solution washed with saturated sodium bicarbonate solution until neutral, followed by a brine wash. The ether layer was dried by filtration through anhydrous sodium sulfate, followed by treatment with 3A molecular sieves. Evaporation of the solvent left a residue of crude product, 17.4 g (100%), $[\alpha]^{25}D$ −38.3° (*c* 4.68, $CHCl_3$). Analytical glpc (Carbowax, 170°) indicated a 28:72 ratio of isomers. Very careful fractional distillation on a Nester-Faust Auto-Annular spinning band column [rate of distillation 0.5–1.5 ml/hr, bp 92–94° (1.5–1.8 mm)] permitted partial separation of the trans–cis mixture into fractions 88% trans, $[\alpha]^{25}D$ +67.6° (*c* 4.66, $CHCl_3$), and 98% cis, $[\alpha]^{25}D$ −79.8° (*c* 5.30, $CHCl_3$). Combination of these fractions with others previously prepared, and further fractional distillation as above permitted isolation of a 8.18-g fraction of (+)-5 (95% trans): $[\alpha]^{25}D$ +73.5° (*c* 4.78, $CHCl_3$); nmr 2.10–3.00 (5, m, ring H's and H adjacent to carboxyl), 1.02 and 1.18 (6, s, ring methyls), 1.99 (3, s, acetyl methyl), and 3.55 ppm (3, s, methyl ester). Another fraction, 76% cis, $[\alpha]^{25}D$ −42.6° (*c* 4.93, $CHCl_3$), was obtained as forerun.

The optical purity and maximum rotation of (+)-*trans*-4 was determined from carefully purified (−)-*cis*-3 (98.6% optically pure). Esterification gave the expected mixture of diastereomers which was separated into two fractions by careful distillation. The rotations found for each fraction are listed in Table I. By solving the simultaneous equations

$$0.88[\alpha_t]D + 0.12[\alpha_c]D = +67.6°$$

$$0.02[\alpha_t]D + 0.98[\alpha_c]D = -79.8°$$

pure (+)-*trans*-4 was calculated to have $[\alpha]D$ −89°. On a larger scale, a sample of *trans*-11 (95%) distilled from a combination of several runs, had a specific rotation $[\alpha]D$ +73.5°, and a forerun of *cis*-11 (76%) had $[\alpha]D$ −42.6°. By solving simultaneous equations similar to those above, a value of $[\alpha]D$ +81.7° was obtained for the *trans*-11 from this batch, corresponding to an optical purity of 91%. The sequence of reactions used to prepare *trans*-11 from α-pinene only permits epimerization of C_3; therefore, the trans isomer must be predominantly the 1*R*,3*S* enantiomer.

(+)-Methyl *trans*-(3-Acetoxy-2,2-dimethylcyclobutyl)acetate [(+)-*trans*-5]. The 8.18 g (0.042 mol) of (+)-*trans*-4 (95% trans) obtained above and 10.2 g 85% *m*-chloroperbenzoic acid (8.63 g pure, 0.500 mol) (Columbia Organic Chemicals) were dissolved in 100 ml of $CHCl_3$ in a 250-ml round-bottomed flask which was wrapped with aluminum foil to exclude light. The resulting solution was allowed to stand at ambient temperature for 5 days, at which time the flask had become filled with precipitated *m*-chlorobenzoic acid. Analytical glpc indicated the reaction was complete. The solution was chilled in an ice bath and filtered to remove most of the *m*-chlorobenzoic acid. The filtrate was washed with a sodium thiosulfate solution to decompose the remaining peracid, and with a sodium carbonate solution to remove the remaining carboxylic acid. Rotary evaporation of the solvent, followed by simple vacuum distillation of the residue, afforded 8.14 g (92%) of (+)-*trans*-5. Analytical glpc (Carbowax, 170°) indicated the product was a 95:5 mixture of isomers, and otherwise pure: $[\alpha]^{25}D$ +6.18° (*c* 5.60, $CHCl_3$); bp 84–87° (1.3 mm); nmr ($CDCl_3$) 1.04 and 1.08 (6, s, methyl groups at C_2), 2.02 (3, s, acetate methyl), 1.9–2.5 (5, m, ring H's and H adjacent to carboxyl), 3.63 (3, s, methyl ester), and 4.4–4.8 ppm (1, m, H at C_3).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.67; H, 8.45. Found: C, 61.80; H, 8.56.

(+)-*trans*-2,2-Dimethyl-3-(2′-hydroxy-2′-methyl-1′-propyl)cyclobutanol [(+)-*trans*-6]. Methylmagnesium iodide was prepared by adding 27.1 g (0.191 mol) of methyl iodide in 160 ml of anhydrous ether to 5.57 g (0.229 mol) of magnesium turnings in 50 ml of anhydrous ether under a nitrogen atmosphere. To the resulting magnetically stirred Grignard reagent was added dropwise in 50 ml of ether, 8.10 g (0.038 mol) of (+)-*trans*-5. The resulting mixture was stirred for 1 hr and then the magnesium salts were precipitated by adding saturated ammonium chloride solution until the solids coagulated. The ether was decanted and the solid residue washed with another 100 ml of ether. The combined ether fractions were washed with 1 *M* hydrochloric acid saturated with ammonium chloride, followed by washing with brine. The solution was dried and the solvent evaporated yielding ~3 g (45%) of a viscous oil. Since most of the product was still occluded in the precipitated magnesium salts, they were dissolved with the minimum of dilute hydrochloric acid (the solution was still somewhat basic, as indicated by the odor of ammonia present). The resulting solution was extracted with several 50-ml portions of ether and the combined ether fractions were treated as above. A total yield of 6.5 g (99%) of syrupy diol was obtained. The portion isolated from the salts, after complete removal of solvent under vacuum, was analytically pure: $[\alpha]^{25}D$ +38.4° (*c* 3.12, $CHCl_3$); nmr ($CDCl_3$) 0.97 and 1.05 (6, s, methyl groups at C_2), 1.18 (6, s, methyl groups at $C_{2'}$), 1.25–2.15 (7, m, H's at C_3, C_4, $C_{1'}$, and hydroxyl), and 3.8–4.0 ppm (1, m, H at C_1).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.70; H, 11.72. Found: C, 69.77; H, 11.52.

(−)-*trans*-2,2-Dimethyl-3-(2′-methylpropenyl)cyclobutanol [(−)-*trans*-7]. In a 100-ml round-bottomed flask with condenser and drying tube were stirred magnetically at 75° (for about 6 hr) a solution of 6.4 g (0.037 mol) of diol (+)-*trans*-6, 15 ml of cyclohexane, 25 ml of anhydrous formic acid (dried by distillation from phthalic anhydride), and *ca.* 5 g of 3Å molecular sieves. The reaction mixture was worked up by diluting with an equal portion of water and extracting with three 50-ml portions of pentane. The combined pentane fractions were washed in succession with a 50-ml portion of brine, saturated bicarbonate until neutral, and a second wash with brine. Filtration through anhydrous sodium sulfate followed by treatment with molecular sieves and removal of solvent on a rotary evaporator gave a light yellow residue. Final purification was by chromatography on 200 g of 10% silver nitrate–silica gel. Elution with 2% ether–pentane (olefin free) gave a 0.065-g fraction of (−)-*trans*-7 (97% trans) followed by 2.00 g of (+)-*trans*-7 (91% trans). Elution of the column with ether yielded 0.6 g of

Table I
Specific Rotations of Mixtures of (1*R*,3*R*)-4 and (1*R*,3*S*)-4

Composition[a]		
% *cis*-4	% *trans*-4	$[\alpha]^{25}D$,[b] deg
12	88	+67.6[c]
98	2	−79.8[c]
5	95	+73.5[d]
76	24	−42.6[d]

[a] Determined on a 500 ft × 0.03 in. Carbowax 20M open tubular column. [b] Taken in chloroform. [c] From small sample of carefully purified (1*R*,3*R*)-4. [d] From combined samples obtained from several runs.

more polar compounds (assumed to be diformate and hydroxyformates) which upon retreatment with formic acid and column chromatography yielded another 0.2 g of (−)-*trans*-**7**. The total yield of (−)-*trans*-**8** was 2.26 g (42%). The 97% trans portion was further purified by preparative gas chromatography: $[\alpha]^{25}D$ −39.0° (*c* 2.18, $CHCl_3$); nmr 1.00 and 1.06 (6, s, methyl groups at C_2), 1.58 and 1.73 (6, doublets, methyl groups at $C_{2'}$, J = 1 Hz), 2.0–3.0 (3, m, H at C_3 and C_4), 4.83 (1, t, H at C_1, J = 7 Hz), 5.15 (1, doublet of septets, H at $C_{1'}$, J = 10, 1 Hz), and 7.91 ppm (1, s, formyl H); high resolution mass spectrum *m/e* calcd for $C_{11}H_{18}O_2$ 182.1306; *m/e* found 182.1256.

(+)-*trans*-2,2-Dimethyl-3-(2′-methylpropenyl)cyclobutanol [(+)-*trans*-1]. A solution of 2.00 g of (−)-*trans*-**7** (11 mmol) in 10 ml of anhydrous ether was added dropwise over a period of 20 min to a magnetically stirred slurry of 0.346 g (36.5 mequiv) of lithium aluminum hydride in 15 ml of anhydrous ether under a nitrogen atmosphere. The resulting mixture was stirred for 2 hr, an additional 30 ml of ether added, and lithium and aluminum salts were precipitated by the dropwise addition of a saturated ammonium chloride solution. The ether was decanted, and the residue washed with another 30 ml of ether. The combined ether fractions were washed in succession with dilute hydrochloric acid, saturated sodium bicarbonate solution, and brine before the solution was dried over 3A molecular sieves. Solvent was removed on the rotary evaporator giving 1.46 g of a colorless oil (86%): $[\alpha]^{25}D$ +6.73° (*c* 4.47, $CHCl_3$); nmr 0.88 and 1.04 (6, s, methyl groups at C_2), 1.53 and 1.69 (6, d, methyl groups at $C_{2'}$, J = 1.5 Hz), 3.26 (1, s, hydroxyl group), 3.82 (1, t, H at C_1, J = 7 Hz), and 4.99 ppm (1, doublet of septets, H at $C_{1'}$, J = 11, 1.5 Hz).[7]

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Registry No.—(+)-*trans*-**1**, 52305-33-6; (−)-**2**, 7785-26-4; (−)-*cis*-**3**, 52305-34-7; (−)-*cis*-**4**, 52305-35-8; (+)-*trans*-**4**, 52305-36-9; (+)-*trans*-**5**, 52259-48-0; (+)-*trans*-**6**, 52259-49-1; (−)-*trans*-**7**, 52259-50-4.

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(8) Although Coates and Robinson[2d,7] have consistently reported the vinyl proton of *trans*-**1** as having an nmr chemical shift upfield from that of *cis*-**1**, we have always found the reverse. Examination of a spectrum reproduced in ref 7 confirms that the chemical shift of the olefinic proton for the minor isomer of the 40:60 mixture, reported to be *trans*-**1**, is indeed downfield from the cis isomer, as we have also found.

Isolation and Properties of Acetyl Hypobromite

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Acyl hypohalites (**1**) are relatively unstable substances which are decomposed by heat or light to form carbon dioxide, alkyl halides, and esters.[1-3] Of the various types which may exist only acetyl hypochlorite[4] and the perfluoroacyl hypofluorites[5] have been isolated in relative purity and characterized.

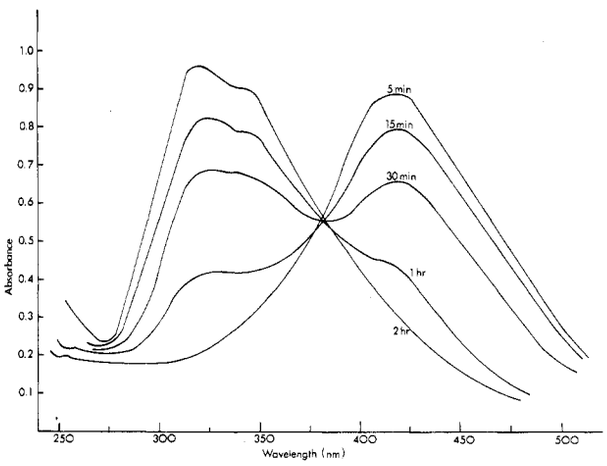
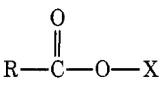


Figure 1. Absorption spectra of filtered acetyl hypobromite solutions (lines indicate extent of nitrogen purge). Initial solution: 0.05 *M* bromine and silver acetate.



1

X = halogen

Acetyl hypobromite has been studied in solution and some properties have been reported. In carbon tetrachloride solution it absorbs in the ultraviolet region with a λ_{max} of 320 nm.[6] An infrared spectrum of the hypobromite in acetic acid shows an absorption at 670 cm^{-1} attributed to the O–Br stretching frequency by analogy with an absorption at the same frequency by *tert*-butyl hypobromite.[7] Hatanaka, Keefer, and Andrews[7] have attempted to isolate acetyl hypobromite by vacuum distillation of its solution in carbon tetrachloride, but no fraction which could be characterized as the hypobromite was detected. Beebe and Wolfe[8] found acetyl hypobromite to be stable in carbon tetrachloride at −15 to 15° for 4 weeks.

On the basis of its relatively high molecular weight and predicted polarity, acetyl hypobromite would be expected to be a high-boiling liquid or a solid. Preparation of the compound in a volatile, inert solvent which could be carefully distilled should lead to its isolation.

Results and Discussion

The reaction of bromine with silver acetate suspended in carbon tetrachloride and nitrogen flushing of any excess bromine (eq 1) yields a dark, green-yellow solution containing acetyl hypobromite. The observed color agrees with that reported by others.[7] Figure 1 shows the uv–visible spectrum of the filtered bromine–silver acetate system at various times of nitrogen purge. The quantitative aspects of the curves would be expected to vary with rate of nitrogen flow but the trends are reproducible in general form. The nitrogen flow is sufficiently slow that the stoichiometric quantity of bromine is not lost. The bromine peak at 415 nm is seen to disappear while a maximum at 320 nm persists along with a shoulder at 340 nm. A similar spectrum is obtained when perfluorinated hydrocarbon is used as solvent in place of carbon tetrachloride, the difference

$$CH_3COOAg + Br_2 \longrightarrow CH_3COOBr + AgBr \quad (1)$$