chloride essentially as described for preparation of related nucleoside derivatives.[12] Compound **1b** was obtained in 85% yield as a white solid melting at 93–98°; λ_{max} (EtOH) 266 nm (ϵ 11,500), λ_{min} 250 nm (ϵ 9650).

Anal. Calcd for $C_{30}H_{29}N_5O_5$: C, 66.78; H, 5.42; N, 12.98. Found: C, 66.35; H, 5.27; N, 13.28.

Compound **1b** (0.27 g, 0.5 mmol) and triphenylphosphine (0.26 g, 1 mmol) were dissolved in pyridine (0.6 ml) at 0°. Concentrated ammonium hydroxide (0.4 ml) was added and the solution was allowed to warm to room temperature. After 2 hr TLC revealed that the azide had reacted completely but the phosphinimine had only partially hydrolyzed to the amine [R_f (CH_2Cl_2–THF 1:1) 0.35 for **1b** and 0.20 for the phosphinimine]. Additional pyridine–ammonia (1 ml, 6:4 v/v) was added and the mixture was allowed to stand overnight, at which time the reaction was complete by the TLC test. Work-up as described for **1c** yielded 0.23 g (88%) of compound **5b**. This sample [R_f (EtOAc) 0.01] contained traces of material with R_f 0 (ninhydrin positive) and R_f 0.47 (positive to perchloric acid spray). Thick layer chromatography on silica gel yielded a pure sample (softened at 100°, completely melted at 114°), λ_{max} (EtOH) 265 nm (ϵ 11,100), λ_{min} 250 nm (ϵ 9190).

Anal. Calcd for $C_{30}H_{31}N_3O_5$: C, 70.16; H, 6.08; N, 8.18. Found: C, 69.89; H, 5.82; N, 8.15.

$d(NH_2)T_p(NH)T_p(NH)T_p(NH)T$ (6). A solution of **4** (16 mg, 0.015 mmol) and triphenylphosphine (43 mg, 0.16 mmol) in pyridine (0.5 ml) was stirred at 25° for 1.5 hr, mixed with water (0.5 ml), and stirred for an additional 2 hr. The solvent was evaporated under reduced pressure, aqueous sodium hydroxide (1.0 ml, 0.2 *M*) was added, and the mixture was stirred overnight. Following extraction with methylene chloride (5 × 2 ml) a small portion of the aqueous layer was analyzed by paper electrophoresis at pH 7.2. A strong spot was observed under ultraviolet light at R_m −0.51 (relative to d_pT), and it was ninhydrin positive; the only other nucleotidic material appeared as a very faint spot (ninhydrin negative) at R_m 0.73, corresponding to a trace of unreacted **4**. The reaction product was separated from the major portion of the solution by chromatography on paper with solvent F. Elution with water, conversion to the triethylammonium salt, and lyophilization afforded 18 mg of **6**, R_f (F) 0.33. Hydrolysis of an aliquot with 80% aqueous acetic acid (15 min on steam bath) yielded $d(NH_2)T$ and $d(NH_2)T_p$ (see Table I for properties) in a ratio of 1:2.8.

Reduction of Azide 2 to Amine 3 with Triphenylphosphine. Compound **2** (10 mg, 0.015 mmol) was added to a solution of triphenylphosphine (10 mg, 0.04 mmol) in pyridine (0.1 ml) and 50% saturated methanolic ammonia (0.1 ml). After 72 hr the solution was concentrated under reduced pressure, and the residue was dissolved in methanol and spotted on Whatman 3MM paper. Development in solvent A yielded **3** as a spot at R_f 0.56 (visualized under uv light, ninhydrin positive). The product was eluted from the paper with tetrahydrofuran and was precipitated from the tetrahydrofuran with hexane. On drying to constant weight, 7.5 mg (78%) of **3** was obtained, mp 139–141° (with softening at 130°). It was identical with **3** (prepared independently by catalytic reduction) on TLC [R_f (THF) 0.12], paper chromatography with solvent A, and paper electrophoresis (R_m −0.4 relative to d_pT, pH 7.2, 0.05 *M* sodium phosphate buffer).

Acknowledgment. This research was supported by the National Institute of General Medical Sciences of the National Institutes of Health (Grant GM 10265).

Registry No.—**1a,** 19316-85-9; **1b,** 54814-97-0; **1c,** 54814-98-1; **2,** 54814-99-2; **2** phenyl phosphorylated, 54815-00-8; **3,** 54815-01-9; **4,** 54815-02-0; **5a,** 25152-20-9; **5b,** 54815-03-1; **5c,** 54815-04-2; **6,** 54815-05-3; phenyl phosphorodichloridate, 770-12-7; naphthyl isocyanate, 86-84-0; mono-*p*-methoxytrityl chloride, 14470-28-1; triphenylphosphine, 603-35-0.

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Dehydration of *erythro*- and *threo*-1,2-Diphenyl-1-propanol with Iodine, *p*-Toluenesulfonic Acid, and Methyltriphenoxyphosphonium Iodide

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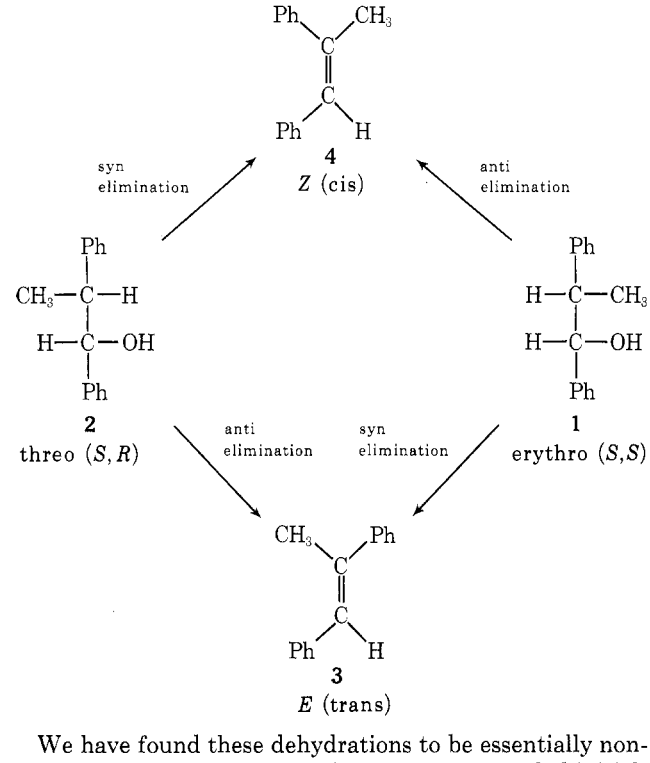
Received November 12, 1974

Iodine has long been used as a catalyst for the dehydration of secondary alcohols,[1,2] including diacetone alcohol,[1,3] and tertiary alcohols,[1,2] including pinacols.[1,4] Little is known about why iodine has this remarkable catalytic activity and nothing is known about the stereochemistry of iodine-catalyzed dehydrations. We have studied the dehydration of the erythro (**1**) and threo (**2**) isomers of 1,2-diphenyl-1-propanol to determine the stereochemistry of the reaction.



We have found these dehydrations to be essentially nonstereospecific. In both cases the reaction proceeded initially with about 55% anti-periplanar elimination. This was followed by equilibration to the equilibrium mixture consisting of 72% *E*- (**3**) and 28% *Z*-α-methylstilbene (**4**). The threo alcohol (**2**) dehydrated more rapidly than its erythro isomer.

The *p*-toluenesulfonic acid (PTSA) catalyzed dehydration of **1** and **2** in refluxing *p*-xylene was also found to proceed initially in a nonstereospecific manner followed by equilibration of **3** and **4** on longer heating. As with the iodine-catalyzed reaction, the threo alcohol dehydrated more rapidly than the erythro isomer. With both iodine and PTSA our results are consistent with the formation with a common intermediate carbonium ion, but are insufficient

to prove this mechanism. Manas and Villa[2] have demonstrated the absence of a common intermediate carbonium ion in a related case. These authors dehydrated *erythro*- and *threo*-2,3-diphenyl-2-butanol (**5**) using either iodine or PTSA in refluxing benzene, and obtained *cis*- and *trans*-α,α'-dimethylstilbene (**6**) and 2,3-diphenyl-1-butene (**7**) in the following amounts: from *erythro*-**5** with iodine, 62% *cis*-**6**, 27% *trans*-**6**, and 11% **7**; from *threo*-**5** with iodine, 10% *cis*-**6**, 4% *trans*-**6**, and 86% **7**; from *erythro*-**5** with PTSA, 41% *cis*-**6**, 18% *trans*-**6**, and 41% **7**; from *threo*-**5** with PTSA, 48% *cis*-**6**, 50% *trans*-**6**, and 2% **7**. The different product distribution from the erythro and threo compound rules out a common intermediate.

Recently, Hutchins et al.[5] have pointed out the usefulness of methyltriphenoxyphosphonium iodide in hexamethylphosphoramide (HMPA) for the selective dehydration of secondary alcohols; so it seemed desirable to try this reagent with alcohols **1** and **2** to determine the stereoselectivity of this method of preparing olefins. The reaction is believed to involve the initial replacement of the hydroxyl group by iodine with inversion, followed by dehydroiodination induced by the HMPA solvent and iodide ion.[5] We find the mixture of olefins to be formed almost quantitatively and to consist of 64–72% of the less stable *Z* olefin, irrespective of the stereochemistry of the starting alcohol. This strongly suggests that some common intermediate is involved in the reaction. Equilibration is probably occurring at the intermediate iodide stage, since Hutchins et al.[5] observed equilibration at this stage in the dehydration of *cis*-4-*tert*-butylcyclohexanol. These authors also studied the dehydration of 1,2-diphenylethanol (which does not exist in diastereoisomeric forms), and found that it formed (99%) the more stable (*E*)-stilbene. This demonstrates that the more stable olefin is formed by this reaction sequence when structural features allow both possibilities. With our alcohols, the predominate *Z* olefin is formed from the erythro iodide, assuming anti-periplanar elimination. The threo alcohol forms the erythro iodide, and the threo alcohol therefore is expected to form the larger amount of the *Z* olefin, as observed, if complete equilibration is not attained at the iodide stage. In any event, the reaction is partially stereoselective.

Cram[6] first studied the equilibration of olefins **3** and **4** and concluded, on the basis of uv spectra, that the equilibrium mixture contained at least 98% of the *E* isomer (**3**). Manas and Vila[2] isomerized **3** with PTSA, analyzed the products by GLC, and concluded that the equilibrium mixture consisted of 79% of **3**. We used PTSA to equilibrate the olefins by refluxing **3** and **4** in *p*-xylene for up to 44 hr. The equilibrium composition was approached from each side and found by GLC to be 70–73% *E* (**3**) with the balance being the *Z* isomer (**4**).

Our work has demonstrated that (1) the dehydration of alcohols **1** and **2** with either iodine or PTSA is essentially nonstereospecific; (2) the new reagent for selectively dehydrating secondary alcohols, methyltriphenoxyphosphonium iodide, is not stereospecific; the same olefin mixture rich in the less stable *Z* isomer (70%) is obtained from either the erythro or threo alcohols **1** or **2**.

Experimental Section

Melting points are corrected. The infrared spectra were determined with a Perkin-Elmer Model 337 spectrophotometer; the ultraviolet spectra with a Cary 15; and the NMR spectra with a Varian Model A-60. Chemical shift values are expressed as δ values (parts per million) downfield from tetramethylsilane internal standard. GLC analyses were carried out on a Hewlett-Packard Model 5750 research chromatograph with a disk integrator.

***threo*-1,2-Diphenyl-1-propanol** (**2**) was prepared by Cram's method[7] starting with 12 g of magnesium, 78 g of bromobenzene, and 54 g of technical 2-phenylpropionaldehyde which had been freshly distilled, bp 72–73° (6.6 mm). This gave 71 g (70%) of a colorless oil, bp 112–118° (7–8 mm). The product was further purified by conversion to the *p*-nitrobenzoate, which was crystallized seven times from ethyl acetate, mp 143–144°.[7] The ester was hydrolyzed to give the alcohol by refluxing the ester (25 g) in methanol (50 ml) and water (50 ml) with sodium hydroxide (3.1 g) for 12 hr: bp 136–138° (1.5 mm) [lit.[7] bp 136–137° (1–2 mm)]; ir identical with literature spectrum;[8a] NMR (CCl_4) δ 4.52 (d, 1, J = 6 Hz, >CHOH), 2.90 (m, 1, >C**H**CH_3), 2.30 (s, 1, –OH), 1.18 (d, 3, J = 7 Hz, –CH_3).

***erythro*-1,2-Diphenyl-1-propanol** (**1**). 1,2-Diphenyl-1-propanone was first prepared by a chromic acid oxidation of **2**.[7] The crude ketone was hydrogenated over W-2 Raney nickel at 100° and 70 atm pressure. NMR analysis showed nine parts of **1** to one part of **2** in the product. Crystallization from "isooctane" gave crystals: mp 48–49° (lit.[7] mp 50–51°); ir identical with literature value;[8b] NMR (CCl_4) δ 7.10 (m, 10, Ph), 4.43 (d, 1, J = 8 Hz, CHOH), 2.87 (m, 1, >C**H**CH_3), 2.20 (s, 1, –OH), 1.00 (d, 3, J = 7 Hz, –CH_3).

***(E)*-α-Methylstilbene** (**3**). A pure sample, mp 80–81° (lit.[7] mp 81–82°), was prepared by the low-temperature pyrolysis of the methyl xanthate of **1** according to Cram's method:[7] uv max (95% C_2H_5OH) 274 nm (ϵ 20,400) [lit.[7] 273 nm (ϵ 19,900)]; ir identical with literature;[8c] NMR (CCl_4) δ 7.25 (m, 10, Ph), 6.75 (broad d, 1, >CH–), 2.42 (d, 3, J = 1.5 Hz, –CH_3).

***(Z)*-α-Methylstilbene** (**4**). We could not obtain **4** by the preceding procedure starting with **2**; our modified procedure follows. Five grams of **2** was dissolved in 60 ml of toluene and 25 ml of the toluene was distilled off. Metallic potassium (0.75 g) was added and the mixture was refluxed for 1 hr. Carbon disulfide (3.5 g) was added, and the mixture was heated with stirring for 10 hr. Methyl iodide (8 g) was added and the solution was refluxed for an additional 2.5 hr. At the end of this time the mixture was shaken with 100 ml of 1:1 water–ether. The ether layer was washed with three 35-ml portions of water and the solvents were removed under water-pump pressure, leaving a yellow-orange oil. This was heated to around 180° at water-pump pressure to pyrolyze the xanthate and distil off the olefin. The portion that distilled was a pale yellow oil (1.6 g), which could not be induced to crystallize. Injection of a sample of the oil in a F & M Model 300 GLC chromatograph (silicon gum rubber column at 160°) revealed three major peaks with retention times of 8.7, 11.9 (**4**), and 21.9 (**3**) min in the ratio 20:35:45. The properties of the GLC-purified **3** follow: ir, identical with literature;[8d] NMR (CCl_4) δ 7.00 (m, 10, Ph), 6.40 (broad d, 1, >CH–), 2.13 (d, 3, J = 1.5 Hz, –CH_3). The uv spectrum was obtained on another sample known from GLC analysis to be 85% **4** and 15% **3**: uv max (95% C_2H_5OH) 263 nm (ϵ 11,800) [lit.[7] 262 nm (ϵ 11,700)].

General Procedure Using Iodine. In a 50-ml round-bottom flask were placed 5–50 mg of iodine, 200 mg of **1** or **2**, and 10 ml of *p*-xylene. This mixture was heated at reflux for 1 hr and then allowed to cool. Sodium thiosulfate solution (10 ml) was added to the solution, and the mixture was stirred for 5 min. The layers were separated and the organic layer was concentrated on a rotary evaporator to a yellow oil. This was chromatographed on 30 g of silica gel (Brinckman, 70–325 mesh), using cyclohexane as the el-

Table I
Dehydration of 1,2-Diphenyl-1-propanol

Stereoisomer	Reagent (mg catalyst/g alcohol)[a]	Time, hr	% yield of 3 + 4	Composition of mixture	
				% *E* (3)	% *Z* (4)
1	Iodine[a] (250)	1	19	43	57
1	Iodine[a] (260)	3	95	73	27
2	Iodine[a] (250)	1	82	54	46
2	Iodine[a] (240)	3	83	70	30
2	Iodine[b] (21)	1	50	45	55
1	PTSA[a] (44)	3	95	53	47
2	PTSA[a] (44)	3	95	72	28
1	MTPI[c]	1	95	36	64
2	MTPI[c]	1	95	28	72

[a] In refluxing *p*-xylene at 138°. [b] No solvent; temperature was 150°. [c] Followed procedure of ref 5; the methyltriphenoxyphosphonium iodide in excess was heated with the alcohol at 80° in hexamethylphosphoramide for 1 hr.

uent. The cyclohexane was removed from each fraction at water-pump pressure, and the residues were weighed. The fractions were as follows. Fraction 1 (70 ml) contained no olefins and was discarded. Fraction 2 (450 ml) contained 150 mg of the two olefins and no starting material. Fraction 3 (100 ml) contained neither olefins nor starting alcohol and was discarded. Fraction 4 (200 ml) contained 58 mg of material, primarily the starting alcohol and no olefins. Samples of fractions 2 and 4, dissolved in a little cyclohexane, were analyzed by GLC (silicon gum rubber column at 180°). The *Z* olefin had a retention time of 7.8 min while the *E* olefin had a retention time of 13.6 min. The results are tabulated in Table I.

General Procedure Using PTSA. Compound **2** (250 mg), 12 mg of PTSA monohydrate, and 5 ml of *p*-xylene were heated with refluxing for 3 hr. The mixture was allowed to cool to room temperature and washed with 20% sodium carbonate solution and water. After removal of the solvent the NMR spectrum showed no indication of starting alcohol. Accordingly, the chromatography on silica gel was omitted. The olefin mixture was analyzed by GLC as before and the results are in Table I.

General Procedure Using Methyltriphenoxyphosphonium Iodide. This followed ref 5. Compound **2** (296 mg), 1.86 g of methyltriphenoxyphosphonium iodide, and 9 ml of dry hexamethylphosphoramide (dried over calcium hydride and stored over molecular sieves 4A) were heated in an oil bath at 80° for 1 hr. The reaction mixture was poured over 20 ml of 10% potassium hydroxide solution and extracted with four 10-ml portions of cyclohexane. These were washed with water and dried ($MgSO_4$), the solvent was removed, and the oil was analyzed by NMR and GLC. The results are in Table I.

Equilibration of 3 and 4. Olefin **3** (315 mg) was refluxed with 13 mg of PTSA monohydrate in 10 ml of *p*-xylene. Samples were removed for analysis of the *E* and *Z* olefins from time to time, and injected directly into the GLC. The results were as follows (hr, % **3**): 0, 100; 0.5, 88; 1.0, 79; 3.0, 78; 20, 73.

The experiment was repeated with 109 mg of **4** (containing 15% of **3**) and 6 mg of PTSA in 4 ml of refluxing *p*-xylene. The results were as follows (hr, % **3**): 0, 15; 0.5, 17; 1.0, 21; 1.5, 39; 2.0, 44; 4.0, 50; 24.0, 61; 44, 70.

Registry No.—**1**, 7693-84-7; **2**, 7693-85-8; **3**, 833-81-8; **4**, 1017-22-7; iodine, 7553-56-2; *p*-toluenesulfonic acid, 104-15-4; methyltriphenoxyphosphonium iodide, 17579-99-6; triphenoxymethyliodophosphorane, 4167-91-3.

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Selective Oxidation of Allylic Alcohols with Chromic Acid

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Received January 17, 1975

Although examples of synthesis of aldehydes by oxidation of primary alcohols with chromic acid reagents are in the literature, many reviews and advanced texts[1] suggest that other reagents (chromic anhydride–pyridine, activated manganese dioxide) or special conditions (removal of aldehyde as it is formed) are necessary for effecting this conversion in high yields. This note demonstrates that primary allylic alcohols can be converted to the corresponding α,β-unsaturated aldehydes in high yield using chromic acid in acetone (Jones reagent).[2]

In other synthetic work[3] we had observed that some α,β-unsaturated aldehydes were inert to normal conditions for Jones oxidation. Although an extensive investigation of the reaction did not seem warranted, we have examined the behavior of some simple primary allylic alcohols upon treatment with Jones reagent.

The oxidation of cinnamyl alcohol to cinnamaldehyde has frequently been cited as an illustration of the utility of the chromic anhydride–pyridine complex.[1a,c] Holum[4] obtained cinnamaldehyde in 87% yield using the complex. We found that simple oxidation with Jones reagent gave the aldehyde in an 84% yield.[5]

Geraniol and nerol were used as examples of simple terpenoid primary allylic alcohols. Treatment of these alcohols with Jones reagent gave aldehydes in high yield. Geraniol was converted into aldehyde in a 91% yield. However, GLC investigation showed that a small amount of isomerization of the double bond had occurred. The GLC data indicated that the product consisted of about 96% geranial and 4% neral. Oxidation of 95% nerol gave aldehyde in 84% yield, and GLC indicated that isomerization had occurred to the extent of about 8%. Thus the oxidation with Jones reagent does have the disadvantage of causing some loss of double-bond stereochemistry in these two cases.

Oxidation of benzyl alcohol to benzaldehyde with Jones reagent also proceeded in good yield, although this reaction appeared more sensitive to experimental variations than the other oxidations. Thus benzaldehyde was obtained in 76% yield using Jones reagent.

These results demonstrate that oxidation of allylic or benzylic alcohols to the corresponding aldehydes occurs using the simple Jones oxidation procedure without the need to use large amounts of expensive activated manganese dioxide or to use a chromic acid–pyridine reagent.

Experimental Section

Proton NMR spectra were recorded on a Varian T-60 spectrometer employing tetramethylsilane as an internal standard and CCl_4 as a solvent. The ir spectra were recorded on a Beckman IR-8 spectrophotometer. GLC analyses were performed on a Hewlett-Packard 700 gas chromatograph using an SE-30 column (6 ft × 0.1875 in., 10% on Chromosorb W) and a Carbowax 20M column (6 ft × 0.1875 in., 10% on Chromosorb W).

The products from the oxidations were identified by comparison of the ir and NMR spectra with spectra of authentic samples or with spectra recorded in the literature.

Jones Oxidation of Cinnamyl Alcohol. A solution of 500 mg (3.72 mmol) of cinnamyl alcohol and 10 ml of reagent-grade acetone was placed in a 50-ml round-bottom flask under nitrogen and cooled to 0° (ice–water bath). To the magnetically stirred solution was added dropwise a solution consisting of 2 ml of 8 *N* Jones reagent and 18 ml of reagent acetone. The Jones solution was added over a period of ca. 20 min until an orange tint persisted in the reaction mixture. Isopropyl alcohol was then added dropwise to destroy excess Jones reagent, as indicated by the reappearance of a deep green color. The reaction mixture was then extracted twice with ether, and the combined ether extracts were washed (water, sodium bicarbonate, and brine), dried over anhydrous magnesium sulfate, and concentrated. Evaporative distillation (0.1 mm, 100°) yielded 420 mg (2.96 mmol, 84%) of a cinnamon-smelling, pale yellow oil (>92% pure by GLC) identified as cinnamaldehyde by comparison of the ir and NMR spectra with literature spectra.

Jones Oxidation of Geraniol. A solution of 500 mg (3.24 mmol) of 99+% geraniol and 10 ml of reagent-grade acetone was placed in a 50-ml round-bottom flask and cooled to 0° (ice–water bath). This solution was treated with Jones reagent in the manner described above. Evaporative distillation of the crude product (0.1 mm, 100°) yielded 450 mg (2.92 mmol, 91%) of a light yellow oil having a citrus odor. GLC (Carbowax) showed 96% geranial and 4% neral as the only significant (>94%) components. The ir and NMR