by a Dry Ice bath. A slow stream of ammonia was bubbled through the mixture for 24 hr. as it warmed to room temperature. The reaction mixture was concentrated under reduced pressure, poured into 300 ml. of 20% sodium hydroxide, and extracted repeatedly with ether. The ether was dried, treated with hydrogen chloride, and the amine hydrochlorides removed. The ether gave 7.5 g. of starting chloride. The amine hydrochlorides were converted to the free amines and distilled to give 19.8 g. (11%) of 3,3-dichloro-2-methylallylamine, b.p. 38° at 1.1 mm. and 114.3 g. (69%) of bis-(3,3-dichloro-2-methylallyl)amine, b.p. 97° at 0.2 mm.

The benzenesulfonamide of the primary amine was recrystallized from ethanol, m.p. 72–74°. Reported value[7] is m.p. 72–74°.

The acetamide of the secondary amide was prepared from acetic anhydride and bis(3,3-dichloro-2-methylallyl)amine and distilled at 129° (0.01 mm.), n_D^{20} 1.5344.

The dichloroacetamide of the secondary amine was prepared from dichloroacetyl chloride and bis(3,3-dichloro-2-methylallyl)amine and was recrystallized from petroleum ether (b.p. 60–70°) to give a white solid, m.p. 100.0–102.5°.

The trichloroacetamide of the secondary amine was prepared from trichloroacetyl chloride and bis(3,3-dichloro-2-methylallyl)amine and was recrystallized from ethanol to give a slightly yellow solid, m.p. 56.0–58.5°.

The benzenesulfonamide of the secondary amine was crystallized from ethanol, m.p. 131–132°.

3,3-Dichloro-2-methylallylamine via Gabriel synthesis. The Sheehan and Bolhofer modification[8] of the Gabriel synthesis was used to prepare *N*-(3,3-dichloro-2-methylallyl)-phthalimide. From 190 g. (1.02 moles) of potassium phthalimide and 159.4 g. (1.0 mole) of 1,1,3-trichloro-2-methyl-1-propene was obtained 214 g. (79%) of *N*-(3,3-dichloro-2-methylallyl)phthalimide, m.p. 118–119°. Analyses are in Table I.

The Ing and Manske modification[9] of the Gabriel synthesis was used for the hydrolysis of *N*-(3,3-dichloro-2-methylallyl)phthalimide. From 54 g. (0.2 mole) of the phthalimide was obtained 17.2 g. (61%) of 3,3-dichloro-2-methylallylamine, b.p. 85–87° (50 mm.), n_D^{25} 1.4992.

Bis and tris(3,3-dichloro-2-methylallyl)hydrazine. To 320 g. (2.0 moles) of 1,1,3-trichloro-2-methyl-1-propene in 400 ml. ethanol was added 110 g. (3.44 moles) of anhydrous hydrazine in small portions during 1 hr. The reaction was heated at 60° for an additional hour. After cooling, the solid was separated and identified as hydrazine hydrochloride, m.p. 87–89°. The alcohol solution was concentrated under reduced pressure and poured into 5% hydrochloric acid. The solid which separated was washed with 4500 ml. of hot water and was crystallized from ethanol. The solid was identified as tris(3,3-dichloro-2-methylallyl) hydrazine, m.p. 90–91°. Analyses are in Table I.

The hot water washes and the acid solution were combined, made basic with sodium hydroxide, and extracted repeatedly with ether. The ether was dried and distilled to give 101.8 g. (37%) of bis(3,3-dichloro-2-methylallyl hydrazine, b.p. 109–115° (0.2 mm.) and an undistilled solid in the distilling flask. The distillate decomposed rapidly to resinous products but was stable as the hydrochloride salt, m.p. 143–145°. Analyses are in Table I.

This compound was believed to be the symmetrical isomer (see discussion).

The undistilled portion was dissolved in boiling petroleum ether (b.p. 60–70°) and on cooling gave two crystalline forms. These crystals were hand separated: 29.0 g. of hard square plates, m.p. 88°, identical with the tris(3,3-dichloro-2-methylallyl)hydrazine isolated above; 24.0 g. of soft fine needles which were tris(3,3-dichloro-2-methylallyl)hydrazine hydrochloride, m.p. 164–165°. Total yield of the trisubstituted hydrazine was 31%.

Anal. Calcd. for $C_{12}H_{17}Cl_7N_2$: Cl^- 8.11; Cl, 56.75; N, 6.41. Found: Cl, 8.06; Cl, 56.37; N, 6.21.

Acknowledgment. We wish to express our gratitude to The Dow Chemical Company for their financial support of this research.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXVI. The 1-Chloro-2-heptenes and 1-Chloro-4,4-dimethyl-2-pentenes

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The 1-chloro-2-heptenes and the 1-chloro-4,4-dimethyl-2-pentenes have been synthesized, characterized, and their relative reactivities toward potassium iodide in acetone and sodium ethoxide in ethanol determined. The data indicate that the rate of reaction is influenced more by the steric requirements imposed by the nature of the group in the *gamma* position of allyl chloride than by inductive effects. Energies and entropies of activation have been calculated for the reaction of the 1-chloro-4,4-dimethyl-2-pentenes with both of these reagents.

The relative reactivities of various methyl substituted allylic chlorides toward potassium iodide in acetone and sodium ethoxide in ethanol have been reviewed by Hatch and Noyes.[2] This area of research has now been extended to include the 1-chloro-2-heptenes (γ-*n*-butylallyl chlorides) and the 1-chloro-4,4-dimethyl-2-pentenes (γ-*tert*-butylallyl chlorides) in order to evaluate further the influence of steric factors on these reactions. A similar study has been made by Bartlett and Rosen on the effect of *n*-butyl and *t*-butyl groups for the reaction between potassium iodide in ace-

(1) Present address: American Alcolac Corporation, Baltimore 26, Md.

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tone and 1-bromo-2-heptyne and 1-bromo-4,4-dimethyl-2-pentyne.[3]

cis-1-Chloro-2-heptene was prepared by the reaction between the corresponding alcohol and phosphorus trichloride.[4] The alcohol was synthesized by the catalytic hydrogenation of 2-heptyn-1-ol using palladium on barium sulfate.[5] The acetylenic alcohol was obtained by the method of Newman and Wotiz.[6] *trans*-1-Chloro-2-heptene was prepared in a similar manner from *trans*-2-hepten-1-ol by use of sodium in liquid ammonia for the reduction.[7,8,9]

The 2-hepten-1-ols have been reported[10,11] but the pure isomers were not isolated. Smets[11] obtained a mixture containing 10% *trans*-2-hepten-1-ol and 90% *cis*-2-hepten-1-ol as indicated by Raman spectra. His claim for pure *trans*-2-hepten-1-ol is based on a stereospecific allylic rearrangement to give only the *trans* isomer. The purity of this alcohol is questioned. Smets prepared the chlorides corresponding to these alcohols. He reported obtaining a mixture containing 25% of the *trans* isomer and 75% of the *cis* isomer. He also reported the preparation of pure *trans*-1-chloro-2-heptene.

The estimation of purity for all of the alcohols and chlorides prepared in the present study is based on their physical properties, infrared spectra, and the melting points of their 3,5-dinitrobenzoates and mixture melting points.

The preparation of both isomers of 1-chloro-4,4-dimethyl-2-pentene by the chlorination of *cis*- and *trans*-4,4-dimethyl-2-pentene with *tert*-butyl hypochlorite has recently been reported.[12] Apparently a mixture of isomers was obtained; detailed physical data were not given. Vernon has utilized 1-chloro-4,4-dimethyl-2-pentene in a kinetic study but neither the method of its preparation nor its geometrical configuration was given.[13]

The 1-chloro-4,4-dimethyl-2-pentenes used in the present investigations were synthesized by an extension of the procedure of Bartlett and Rosen for the production of 4,4-dimethyl-2-pentyn-1-ol. *trans*-4,4-Dimethyl-2-penten-1-ol was obtained by stereospecific reduction *via* the sodium-ammonia method. The *cis* isomer was prepared by catalytic reduction using both Raney nickel[14] and palladium on calcium carbonate.[8,9,15,16] Infrared spectra and physical properties showed the compounds obtained by either catalyst to be identical. The palladium catalyst is recommended for this stereospecific reduction, however, because of the several operational problems inherent in the use of Raney nickel for this reaction.

The 4,4-dimethyl-2-penten-1-ols were converted to the corresponding chlorides by the use of phosphorus trichloride in the presence of a *small* amount of pyridine[4] and by the reaction between the alcohol and thionyl chloride. The infrared spectra of the chlorides prepared by both methods were essentially identical. The infrared spectrum of the *trans* chloride prepared using thionyl chloride, however, indicated the presence of both a terminal double bond (10.8 μ) and a carbon-carbon triple bond (4.59 μ). These compounds could have been formed by an initial S_Ni' reaction[17] to give 3-chloro-4,4-dimethyl-1-pentene which dehydrochlorinated to *tert*-butylallene. The allene could then rearrange to the corresponding acetylene. There was no allene absorption (5.10 μ). The phosphorus trichloride method is more applicable for the preparation of primary allylic chlorides.

The rate constants for the reaction between *cis*- and *trans*-1-chloro-2-heptene and *cis*- and *trans*-1-chloro-4,4-dimethyl-2-pentene and potassium iodide in acetone were determined at 20° for the γ-*n*-butylallyl chlorides and 10°, 20°, and 30° for the γ-*tert*-butylallyl chlorides. Similar data were obtained for their reaction with sodium ethoxide in ethanol at 50° and at 40°, 50°, and 60°, respectively. These kinetic data and relative reactivities are in Table I.

Vernon has published the results of a kinetic investigation of the reaction between a series of allylic chlorides and sodium ethoxide in ethanol at 44.6°. The relative reactivity of an uncharacterized 1-chloro-4,4-dimethyl-2-pentene obtained from these data is 1.96. From this datum it would appear that Vernon used a mixture of the geometrical isomers of 1-chloro-4,4-dimethyl-2-pentene. This conclusion is substantiated by the reported physical properties [b.p. 63.4–63.6° (58 mm.), n_D^{25}, 1.4390]. The conclusions drawn from the kinetic data of Vernon by DeWolfe and Young[17] in respect to the influence of substituents on the γ-carbon atom of allyl chloride are still valid, however. Both

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TABLE I

REACTION RATES AND RELATIVE REACTIVITIES OF CERTAIN γ-BUTYLALLYL CHLORIDES

Compound	k, l. mole^{-1} hr.$^{-1}$			Relative Reactivity[a]
	10°	20°	30°	20°
REACTION WITH POTASSIUM IODIDE IN ACETONE				
cis-1-Chloro-2-heptene		5.37 ± 0.03		10.7
trans-1-Chloro-2-heptene		1.19 ± 0.02		2.37
cis-1-Chloro-4,4-dimethyl-2-pentene	1.19 ± 0.015	2.97 ± 0.03	8.41 ± 0.16	5.92
trans-1-Chloro-4,4-dimethyl-2-pentene	0.24 ± 0.005	0.692 ± 0.007	2.00 ± 0.02	1.38
REACTION WITH SODIUM ETHOXIDE IN ETHANOL				
	40°	50°	60°	50°[b,c]
cis-1-Chloro-2-heptene		3.66 ± 0.07		3.13
trans-1-Chloro-2-heptene		3.15 ± 0.08		2.77
cis-1-Chloro-4,4-dimethyl-2-pentene	0.721 ± 0.05	1.83 ± 0.02	4.38 ± 0.13	1.55
trans-1-Chloro-4,4-dimethyl-2-pentene	1.03 ± 0.01	2.75 ± 0.03	7.15 ± 0.05	2.33

[a] Allyl chloride as 1.00 with k = 0.502. [b] Allyl chloride as 1.00 with k = 1.18. [c] Vernon [*J. Chem. Soc.*, 4462(1954)] reported a relative reactivity of 1.96 for an uncharacterized 1-chloro-4, 4-dimethyl-2-pentene with sodium ethoxide in ethanol at 44.6°.

isomers of γ-*tert*-butylallyl chloride are less reactive than either isomer of γ-methylallyl chloride (crotyl chloride). The *trans* isomer of γ-*tert*-butylallyl chloride is 1.5 times more reactive than the *cis* isomer toward sodium ethoxide but the *cis* isomer is 4.3 times more reactive than the *trans* isomer with potassium iodide. It is apparent that the difference between these isomers not only depends on the configuration of the allylic chloride but also upon the character of the entering group. This reversal was not observed with the γ-*n*-butylallyl chlorides. They show the expected greater reactivity of the *cis* isomer toward both reagents. The difference in reactivity between the *cis* and the *trans* isomers is larger for the reaction with potassium iodide than it is for the reaction with sodium ethoxide.

Bartlett and Rosen in their work with the butylpropargyl bromides indicate that there is very little difference between the *n*-butyl and the *t*-butyl group for the reaction between the substituted propargyl bromides and potassium iodide in acetone. For the corresponding allylic chlorides when the groups are either *cis* or *trans* to the allylic chlorine atom, the γ-*n*-butylallyl chloride is approximately 1.8 times more reactive than the γ-*tert*-butylallyl chloride.

With both the *n*-butyl and *t*-butyl groups the ratio between the reactivity of the *cis* isomer and the *trans* isomer is approximately 4.4. This difference in reactivity between the geometrical isomers must be steric in nature because the inductive effect is the same for each isomer. The difference between the reactivity of the *n*-butyl and the *t*-butyl groups may be steric or inductive. The large size of the butyl groups in the *cis* position may hinder free rotation of the chloromethyl groups. This is especially true with the *t*-butyl group. This hindrance should be more significant when the entering group is large. This is reflected by the fact that the *cis* derivative is less reactive than the *trans* derivative when sodium ethoxide ion is the reagent. All of these data lead to the conclusion that the electron releasing power of the group in the *gamma* position is not as important as the steric requirements of the group.

The data at three different temperatures for the 1-chloro-4,4-dimethyl-2-pentenes permitted the calculations of the energies of activation and the entropies of activation for their reactions with both reagents (Table II). The energies of activation are essentially the same. The slightly lower energy required for the *cis* isomer indicates that the *trans* form is thermodynamically more stable than the *cis*. The negative values for the entropy of activation indicate that a frequency factor is involved in these reactions. Orientation is required to permit the formation of a transition state. The size and shape of the entering group and the configuration of the allylic chloride are the main factors influencing this orientation.

Similar rate data have been obtained for *gamma* isopropyl, ethyl, and methyl groups and will be published in a subsequent paper.

EXPERIMENTAL

cis-1-Chloro-2-heptene. 2-Heptyn-1-ol. This acetylenic alcohol was prepared from 1-hexyne by the method of Newman and Wotiz.[6] A 44% yield of 2-heptyn-1-ol was obtained: b.p. 57.5° (2mm.); d_4^{20} 0.8868, d_4^{25} 0.8832, d_4^{30} 0.8794; n_D^{20} 1.4530, n_D^{25} 1.4518, n_D^{30} 1.4502; lit.[6] b.p. 98° (28 mm.); d_4^{20} 0.8854; n_D^{25} 1.4523.

cis-2-Hepten-1-ol. *cis*-2-Hepten-1-ol was prepared by the catalytic reduction of 2-heptyn-1-ol using palladium on barium sulfate.[5] The yield was only 45% because of polymerization during the distillation of the 2-hepten-1-ol. Martin, Schepartz, and Dauber also reported polymerization during the distillation of a mixture of 2-hepten-1-ols.[10] The *cis*-2-hepten-1-ol had the odor of new mown hay and the following physical properties: b.p. 59.8–60.0° (4 mm.), d_4^{20} 0.8479, d_4^{25} 0.8436; d_4^{30} 0.8403; n_D^{20} 1.4430, n_D^{25} 1.4414;

TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE 1-CHLORO-4,4-DIMETHYL-2-PENTENES

Isomer	Reagent	T°K	$k \times 10^3$ 1 mole^{-1} sec.$^{-1}$	Ea cal. mole^{-1}	S‡ cal. deg.$^{-1}$ mole^{-1}
cis	KI	283	0.305	17,130	−13.96
trans	KI	303	0.556	18,070	−13.82
cis	C_2H_5ONa	333	1.23	18,400	−12.23
trans	C_2H_5ONa	333	1.97	19,850	−11.56

n_D^{30} 1.4396; lit.[11,18] b.p. 59.8–60.0° (4 mm.); d_4^{20} 0.8481; n_D^{20} 1.44424.

cis-1-Chloro-2-heptene. *cis*-1-Chloro-2-heptene was obtained by the reaction between *cis*-2-hepten-1-ol and phosphorus trichloride plus pyridine.[4] The yield was 48% and the product had the following physical properties: b.p. 48.5–49.5° (15 mm.); d_4^{20} 0.9002, d_4^{25} 0.8963, d_4^{30} 0.8924; n_D^{20} 1.4471, n_D^{25} 1.4448, n_D^{30} 1.4422; lit.[11,19] b.p. 84.5–86.5° (70 mm); d_4^{20} 0.90142; n_D^{20} 1.44685.

trans-1-Chloro-2-heptene. *trans-2-Hepten-1-ol.* The sodium in liquid ammonia procedure of Campbell and Eby[7] and others[8,9] was used for the *trans* hydrogenation of 2-heptyn-1-ol to *trans*-2-hepten-1-ol. A 51% yield of *trans*-2-hepten-1-ol was obtained. It had the odor of new mown hay and the following physical properties: b.p. 57.9–58.1° (4 mm.); d_4^{20} 0.8516, d_4^{25} 0.8486, d_4^{30} 0.8454; n_D^{20} 1.4460, n_D^{25} 1.4442, n_D^{30} 1.4423; lit.[5] b.p. 52.6–52.8° (4 mm.); d_4^{20} 0.84255; n_D^{20} 1.44249.

trans-1-Chloro-2-heptene. The procedure of Juvalla[4] was used to convert *trans*-2-hepten-1-ol to *trans*-1-chloro-2-heptene by use of phosphorus trichloride in the presence of pyridine. The yield was 33% and the product had the following physical properties: b.p. 50.5–51.1° (15 mm.); d_4^{20} 0.8955, d_4^{25} 0.8911, d_4^{30} 0.8869; n_D^{20} 1.4467, n_D^{25} 1.4448, n_D^{30} 1.4420; lit.[11] b.p. 87–89° (70 mm.); d_4^{20} 0.90128; n_D^{20} 1.44745.

cis-1-Chloro-4,4-dimethyl-2-pentene. This allylic chloride was prepared from the corresponding alcohol which in turn was obtained by the catalytic hydrogenation of 4,4-dimethyl-2-pentyn-1-ol. The acetylenic alcohol was synthesized from pinacolone by using the general procedure of Bartlett and Rosen.[3]

Pinacolone. Pinacolone was obtained both by the dehydration of pinacol hydrate[20] (76% yield) and by the reaction between acetic anhydride and *tert*-butylmagnesium bromide[21] (50% yield).

2,2-Dichloro-3,3-dimethylbutane and 2-chloro-3,3-dimethyl-1-butene. A mixture of these two compounds was obtained when pinacolone was treated with phosphorus pentachloride at 0–5° for 12 hr. The yield of 2-chloro-3,3-dimethyl-1-butene was 15% and the yield of the dichloride was 67%. In another run the yields were 37% and 56% respectively. The melting point of the 2,2-dichloro-3,3-dimethylbutane was 151–152.5° (lit.[3,22] m.p. 151–152°). The physical properties of the 2-chloro-3,3-dimethyl-1-butene were: b.p. 97–99°; d_4^{20} 0.8843; d_4^{30} 0.8794; n_D^{20} 1.4251, n_D^{25} 1.4230, n_D^{30} 1.4203; lit.[23] b.p. 95.5° (730 mm.); d_4^{20} 0.8888; n_D^{20} 1.4247.

3,3-Dimethyl-1-butyne (tert-butylacetylene). The methods of deGraef,[24] Ivitzky,[22] and Bartlett and Rosen[3] for the dehydrochlorination of the mixture of 2-chloro-3,3-dimethyl-1-butene and 2,2-dichloro-3,3-dimethylbutane to 3,3-dimethyl-1-butyne were modified by equipping the reaction flask with a reflux condenser maintained at 50°. This permitted the removal of the acetylene without loss of reactants. A temperature of 160° was maintained for 12 hr. and of 200° for 2 hr. The yield of 3,3-dimethyl-1-butyne was 88% and the physical properties were: b.p. 37.0–37.5° (758 mm.); n_D^{20} 1.3750; lit. b.p. 36.4–37.8 (768 mm.)[3]; n_D^{20} 1.37493.[22]

A yield of 84% 3,3-dimethyl-1-butyne was obtained from the treatment of 2,2-dichloro-3,3-dimethylbutane (1.00 mole) with potassium hydroxide (9.52 moles) in a similar manner to that used for the mixture of mono- and dichlorides. Similar treatment of 2-chloro-3,3-dimethyl-1-butene with potassium hydroxide gave a 85% yield of the acetylene.

4,4-Dimethyl-2-pentyn-1-ol. 4,4-Dimethyl-2-pentyn-1-ol was synthesized by treatment of 3,3-dimethyl-1-butyne with ethylmagnesium bromide to produce the acetylenic Grignard compound and treatment of this compound with formaldehyde.[3,6,25] The yield was 74% and the alcohol had the following physical properties: b.p. 49.0–50.0° (5 mm.); d_4^{20} 0.8578, d_4^{25} 0.8542, d_D^{30} 0.8505; n_D^{20} 1.4420, n_D^{25} 1.4401, n_D^{30} 1.4380; lit.[3] b.p. 71.6° (18 mm.); d_4^{22} 0.8565; $n_D^{21.5}$ 1.4427.

cis-4,4-Dimethyl-2-penten-1-ol. 4,4-Dimethyl-2-pentyn-1-ol was reduced to *cis*-4,4-dimethyl-2-penten-1-ol by Raney nickel[14] using the procedure of Campbell and O'Conner.[26] The yield was 55%. The reduction was also carried out using a palladium on calcium carbonate catalyst[15] and standard procedure.[3,9,16] The yield was 55%. Both processes gave an allylic alcohol with the same physical properties which were: b.p. 73.5–74.0° (20 mm.); d_4^{20} 0.8418, d_4^{25} 0.8384, d_4^{30} 0.8352; n_D^{20} 1.4390, n_D^{25} 1.4370, n_D^{30} 1.4351.

Anal.[27] Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.58; H, 11.59.

cis-1-Chloro-4,4-dimethyl-2-butene. *cis*-1-Chloro-4,4-dimethyl-2-pentene was prepared by treating the corresponding alcohol with phosphorus trichloride and pyridine in a manner similar to that used for the preparation of *cis*-1-chloro-2-heptene from *cis*-2-hepten-1-ol. The yield was 50%. The chloride was also produced by the treatment of *cis*-4,4-dimethyl-2-penten-1-ol with thionyl chloride in the presence of a small amount of pyridine.[28,29] The yield was 54%. Both processes gave products with the same physical properties which were: b.p. 58–59° (50 mm.); d_4^{20} 0.8860, d_4^{25} 0.8816, d_4^{30} 0.8771; n_D^{20} 1.4422, n_D^{25} 1.4399, n_D^{30} 1.4374.

Anal. Calcd. for $C_7H_{13}Cl$: C, 63.39; H, 9.88; Cl, 26.73. Found: C, 64.27, H, 9.81; Cl, 25.76.

trans-1-Chloro-4,4-dimethyl-2-pentene. *trans*-1-Chloro-4,4-dimethyl-2-pentene was synthesized from the corresponding

(18) These data were reported for a mixture containing 10% *trans*-2-hepten-1-ol and 90% *cis*-2-hepten-1-ol.

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allylic alcohol which in turn was produced by the *trans* hydrogenation of 4,4-dimethyl-2-pentyn-1-ol.

trans-4,4-Dimethyl-2-penten-1-ol. This alcohol was obtained by the hydrogenation of 4,4-dimethyl-2-pentyn-1-ol with sodium in liquid ammonia in a process similar to that used for the production of *trans*-2-hepten-1-ol from 2-heptyn-1-ol. The yield was 80% and the physical properties were: b.p. 71.2–72.7° (20 mm.); d_4^{20} 0.8325, d_4^{25} 0.8291, d_4^{30} 0.8256; n_D^{20} 1.4380, n_D^{25} 1.4360, n_D^{30} 1.4340.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.69; H, 11.91.

trans-1-Chloro-4,4-dimethyl-2-pentene. trans-1-Chloro-4,4-dimethyl-2-pentene was prepared from *trans*-4,4-dimethyl-2-penten-1-ol by reaction with phosphorus trichloride and with thionyl chloride using the same procedures as used for the preparation of the *cis* isomer. The yields were 48% and 56% respectively. The infrared spectra of the compounds produced by these two methods show some small differences. The product from the thionyl chloride procedure has a peak at 4.6 μ indicating the presence of a carbon-carbon triple bond.

The following physical constants were obtained from the chloride synthesized using phosphorus trichloride: b.p. 59–59.5° (50 mm.); d_4^{20} 0.8826, d_4^{25} 0.8783, d_4^{30} 0.8737; n_D^{20} 1.4410, n_D^{25} 1.4387, n_D^{30} 1.4361.

Anal. Calcd. for $C_7H_{13}Cl$: C, 63.39; H, 9.88; Cl, 26.73. Found: C, 63.50; H, 9.51; Cl, 26.36.

3,5-Dinitrobenzoates. The 3,5-dinitrobenzoates of the alcohols were prepared by standard procedure. The 3,5-dinitrobenzoates of the chlorides were prepared by reaction with the silver salt of 3,5-dinitrobenzoic acid. All melting points are corrected.

2-Heptyn-1-ol: m.p. 61.9–62.9.

Anal. Calcd. for $C_{14}H_{14}N_2O_6$: N, 9.14. Found: N, 8.88.

cis-2-Hepten-1-ol: m.p. 41.1°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: N, 9.08. Found: N, 9.06.

trans-2-Hepten-1-ol: m.p. 56.3–56.8.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: N, 9.08. Found: N, 8.89.

cis-1-Chloro-2-heptene: m.p. 41.0–41.3°.

trans-1-Chloro-2-heptene: m.p. 56.5–56.9°.

cis-4,4-Dimethyl-2-penten-1-ol: m.p. 68–69°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: N, 9.08. Found: N, 9.08.

trans-4,4-Dimethyl-2-penten-1-ol: m.p. 86–86.5°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: N, 9.08. Found: N, 9.27.

cis-1-Chloro-4,4-dimethyl-2-pentene: m.p. 68.5–69°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.08. Found: C, 54.75; H, 5.04; N, 8.97.

trans-1-Chloro-4,4-dimethyl-2-pentene: m.p. 86.5–87°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.08. Found: C, 54.27; H, 5.04; H, 9.05.

Infrared spectra. The infrared spectrum of each of the compounds prepared in this study was obtained. With each compound the spectrum confirmed the assigned structure. Photostatic copies of these spectra are available upon request.

Reaction with potassium iodide in acetone. The procedure used was the same as that described previously.[30] With the usual modified second-order rate equation, the plot of log 5-Z/(5)(1-Z) *vs.* time, where Z is the fraction of potassium iodide have reacted in time t, gave a straight line between 40 and 90% reacted at 20° for *cis*-1-chloro-2-heptene and between 21 and 68% reacted at 20° for *trans*-1-chloro-2-heptene. The rate data are summarized in Table I.

Rate data for *cis*- and *trans*-1-chloro-4,4-dimethyl-2-pentene were obtained at 10°, 20°, and 30°. The plot of log b(a − x)/a(b − x) *vs.* time for the *cis* isomer gave a straight line between 21 and 71% reacted at 10°, between 25 and 74% at 20°, and between 49 and 70% at 30°. The *trans* isomer gave a straight line between 37 and 62% reacted at 10°, between 34 and 72% at 20°, and between 54 and 73% at 30°. Representative rate data are summarized in Table I. Thermodynamic functions calculated from these data are in Table II.

Reaction with sodium ethoxide in ethanol. The procedure used was similar to that described previously.[31] The sodium ethoxide solution was 0.05040M for the reaction of both *cis*- and *trans*-1-chloro-2-heptene. Both chlorides were 0.06345M. The data were calculated using the rate expression for a second-order reaction. A plot of log b(a − x)/$a(b - x)$ *vs.* time gave a straight line for the *cis* isomer between 11 and 56% reacted at 50° and for the *trans* isomer between 19 and 55% reacted at the same temperature. The rate data are summarized in Table I.

Rate data for *cis*- and *trans*-1-chloro-4,4-dimethyl-2-pentene were obtained at 40°, 50°, and 60°. A plot of log b(a − x)/a(b − x) *vs.* time for the *cis* isomer gave a straight line between 30 and 53% reacted at 40°, between 29 and 49% at 50°, and between 50 and 69% reacted at 60°. The *trans* isomer gave a straight line between 39 and 64% reacted at 40°, between 43 and 67% at 50°, and between 53 and 67% reacted at 60°. The concentration used for the *cis* isomer were a(chloride) = 0.1046M and b(NaOH) = 0.04789M at 40°, a = 0.05289M and b = 0.04784M at 50°, and a = 0.05289M and b = 0.04789M, at 60°. The concentration for the *trans* isomer were a = 0.1034M and b = 0.04788M at 40°, a = 0.05259M and b = 0.04784M at 50°, and a = 0.05259M and b = 0.04788M at 60°. Representative rate data are given in Table I. Thermodynamic data are in Table II.

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