The organic layer was washed three times with water, dried, evaporated to an oil and distilled to give 0.40 g. of oil. This material was treated with 0.20 g. of phthalic anhydride and 2 ml. of pyridine at 100° for one hour, cooled and shaken with a mixture of benzene and dilute sulfuric acid (excess). The organic layer was washed with water, dried, evaporated and the oil submitted to distillation; weight of ether 0.27 g.

The material that did not distil was crystallized and recrystallized three times from a mixture of ethyl acetate and petroleum ether to give 32 mg. of acid phthalate of VB; m. p. 126–128°, m. m. p. with an authentic sample, 127–129°.

A sample of this material was mixed with an equal weight of the acid phthalate of VA and the mixture crystallized from ethyl acetate and petroleum ether; m. p. 143–144°, m. m. p. with an authentic sample, 143–144°.

Acknowledgment.—The author wishes to thank Welton Burney for the analyses reported in this paper.

Summary

1. The *p*-toluenesulfonates of the isomers of 3-phenyl-2-pentanol and 2-phenyl-3-pentanol (III, IV, V, VI, IIIA, IVA, VA and VIA) were prepared and submitted to acetolysis, and the mixtures of acetates obtained were hydrolyzed to the respective mixtures of alcohols, of which solid derivatives were prepared. From the *p*-toluenesulfonate of either III or V was obtained a mixture of III and V derivatives, from the *p*-toluenesulfonate of either IV or VI was obtained a mixture of derivatives of IV and VI, from the *p*-toluenesulfonate of either IVA or VIA was obtained a mixture of derivatives of IVA and VIA, from the *p*-toluenesulfonate of IIIA was obtained a mixture of derivatives of IIIA and VB, and from the *p*-toluenesulfonate of VA was obtained a mixture of derivatives of IIIB and VA. These results have been interpreted as constituting evidence that a Wagner–Meerwein rearrangement takes place in each system and in a highly stereospecific manner, and that the stereochemistry of these reactions can be explained only on the basis of carbocyclic, asymmetric ionic intermediates.

2. Additional evidence has been obtained for the relative configurations of the above isomers.

LOS ANGELES, CALIFORNIA RECEIVED MARCH 14, 1949

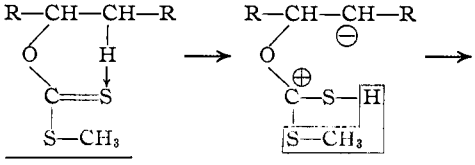
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies in Stereochemistry. IV. The Chugaev Reaction in the Determination of Configuration of Certain Alcohols

BY DONALD J. CRAM

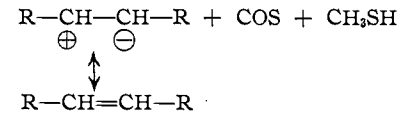
The results of rearrangement studies of the *p*-toluenesulfonates of the isomers of 3-phenyl-2-butanol led in paper I[1] of this series to an assignment of relative configurations to the four stereoisomers. The determination of the relative configurations by an independent method is desirable, and the use of the Chugaev reaction offers not only an attractive and unique method of accomplishing this end, but also offers a means of extending our knowledge of the steric course and mechanism of the Chugaev reaction itself. Since these two problems are completely interdependent, the purpose of this investigation is to show consistency between what is already known about the configurations of the starting material, and what is already known about the stereochemistry of the Chugaev reaction.

Stevens and Richmond[2] have suggested that the lack of rearranged olefins as products of this reaction can be explained by assuming that intramolecular hydrogen bonding prior to the proton elimination takes place, and that the reaction can be pictured as follows.



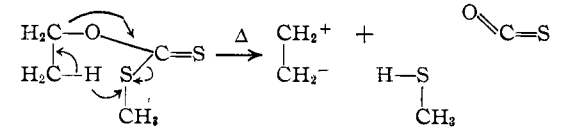
(1) Cram, THIS JOURNAL, **71**, 3863 (1949).

(2) Stevens and Richmond, *ibid.*, **63**, 3132 (1941).



These authors did not state whether the proton was pulled from the carbon before or during the breaking of the carbon oxygen bond, but the diagram implies the former.

Hückel, *et al.*,[3] found that decomposition of the xanthate of *l*-menthol produced about 30% Δ^2-menthene and 70% Δ^3-menthene, and the xanthate of *d*-neomenthol decomposed to give 80% Δ^2-menthene and 20% Δ^3-menthene. Since the hydrogen, loss of which leads to Δ^3-menthene, lies *cis* to the carbon–oxygen bond in the xanthate of *l*-menthol, and *trans* in the xanthate of *d*-neomenthol, the 70% Δ^3-menthene produced by the xanthate of *l*-menthol represents in effect a *cis* elimination reaction, and the 20% Δ^3-menthene obtained from the xanthate of *d*-neomenthol a *trans* elimination reaction. The stereochemistry of the reactions that produced Δ^2-menthene are not clear. These authors interpret the reaction as taking place by a completely concerted proc-



(3) Hückel, Tapp and Legutke, *Ann.*, **543**, 191 (1940).

ess, in which the sulfur bearing the methyl group plucks a proton from the carbon atom adjacent to the carbon atom bearing the oxygen at the same time that the carbon–oxygen and carbon–sulfur bonds break. Such a mechanism can, of course, only apply to a *cis* elimination reaction.

In the present investigation, each of the two racemate series of 3-phenyl-2-butanol when submitted to the Chugaev reaction should give a different geometric isomer of 2-phenyl-2-butene, determination of the structures of which should provide evidence for the relative configurations of the starting carbinols.

Discussion

Preparation, Identification and Characterization of the Isomers of 2-Phenyl-2-butene.—A mixture of the two geometric isomers[4] of 2-phenyl-2-butene was produced by the acid-catalyzed dehydration of 2-phenyl-2-butanol, and the large difference in boiling points permitted separation of the isomers by fractional distillation. If a small amount of *p*-toluenesulfonic acid is added to the pot during fractional distillation, pure *trans* compound[5] can be obtained.

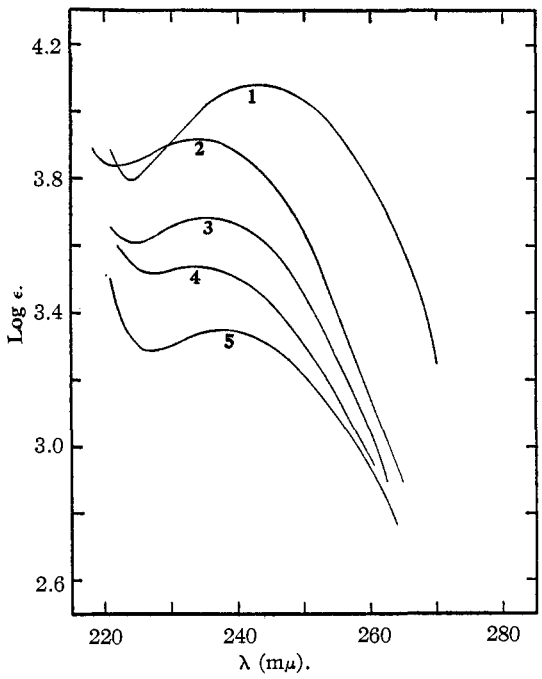


Fig. 1.—Ultraviolet absorption spectra (Beckman quartz spectrophotometer) run in cyclohexane: curve 1, *cis*-2-phenyl-2-butene; curve 2, *trans*-2-phenyl-2-butene; curve 3, fraction A of olefin obtained from xanthate of II; curve 4, fraction A of olefin obtained from xanthate of IV; curve 5, fraction A of olefin obtained from xanthate of I.

(4) If one assumes that the index of refraction of mixtures of these two components is a linear function of the composition, the ratio of the *cis* to *trans* isomer is 4 to 1. This value is roughly verified by the yield data.

(5) This substance, which is the lower boiling isomer, can be distilled from the continually equilibrating mixture.

The molecular structure of each olefin was confirmed by ozonolysis experiments, and the assignment of relative configuration was made on the basis of a comparison of the difference in the ultraviolet absorption spectra (see Fig. 1), and the difference in steric requirements for resonance involving the double bond and the benzene ring that exists between the two substances. Examination of Fisher–Hirschfelder models of each isomer indicates that when the benzene ring and methyl group are on the same side of the double bond (*trans* isomer), rotation of the benzene ring through the position corresponding to coplanarity with the double bond is resisted by interference between the methyl group and the hydrogen at the *o*-position of the ring. When the methyl group is on the opposite side of the double bond (*cis* isomer), this particular resistance to coplanarity is absent. Therefore, a certain amount of steric inhibition of resonance must exist in the *trans* isomer that would not be found in the *cis* compound, and this difference should lead to a divergence in the physical properties of the two substances. Thus the *cis* compound would be expected to be more polar (there should be a greater contribution to the resonance hybrid of dipolar forms in the *cis* than *trans* forms), to boil higher, to have a higher index of refraction and to absorb light at a longer wave length and at higher intensities.[6] Examination of the physical properties (see Experimental) of the two olefins obtained would indicate that the higher boiling substance corresponds to a *cis* (the two methyl groups *cis* to each other) and the lower boiling to a *trans* configuration. The presence of a much higher concentration of the *cis* isomer in an acid equilibrated mixture is consistent with the greater resonance of stabilization expected for the *cis* over the *trans* structure. The difference in free energy amounts to about 520 cal. based on the amounts of each obtained from an equilibrated mixture (the same mixture was obtained from each pure component).

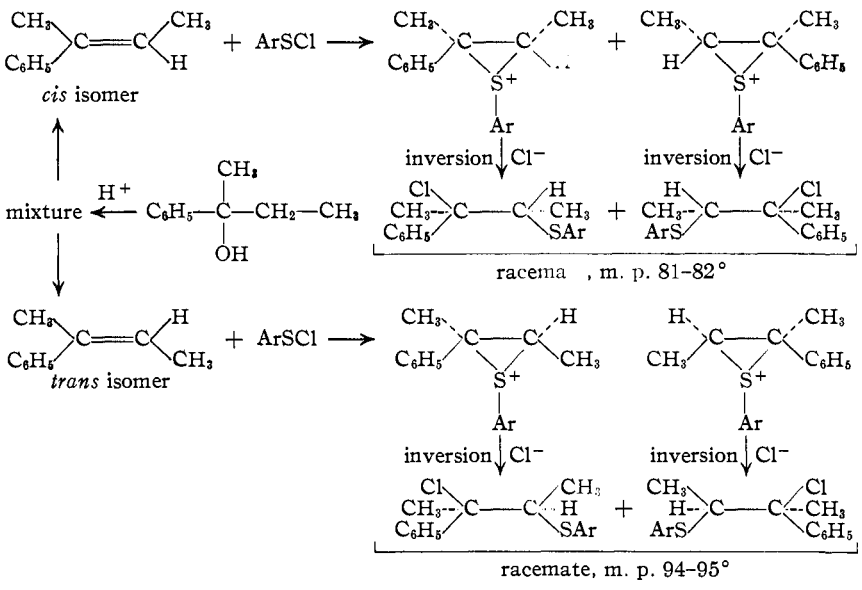
The addition of 2,4-dinitrobenzenesulfenyl chloride[7] to each isomer produced different crystalline derivatives (presumably different racemates), indicating that the addition reaction proceeds in a stereospecific manner. N. Kharasch and Buess[8] have demonstrated that the addition proceeds predominantly according to Markownikoff's rule when conducted in glacial acetic acid, and these authors have suggested a three-membered cyclic cation as an intermediate in the reaction, formed by the addition of 2,4-dinitrobenzenesulfenyl cation to the double bond. The stereospecificity of the reaction found in the present investi-

(6) An example of the effect of steric inhibitions of resonance on absorption spectrum is found in the study of the spectra of *cis*- and *trans*-stilbene by Smakula and Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931).

(7) This reagent, directions for its use and suggestions as to its mode of addition were kindly supplied by Dr. N. Kharasch, University of Southern California.

(8) Kharasch and Buess, THIS JOURNAL, **71**, 2724 (1949).

gation would support this hypothesis, and the course of the reaction can be tentatively formulated as



action which gives rise to 3-phenyl-1-butene. If one assumes on the basis of the findings of Hückel, *et al.*,[3] that the Chugaev reaction is predominantly a *cis* elimination, the above results are substantial proof of the correctness of the configurational assignments of racemates I and II. If one assumes that the configurations of racemates I and II were previously demonstrated by the rearrangement studies (see paper I of this series), then the above results demonstrate that the Chugaev reaction goes predominantly by a *cis* elimination mechanism. In any case, these experiments have linked the two chains of stereochemical evidence together in an internally consistent manner, thereby strengthening each argument.

The Products of the Chugaev Reaction.—The xanthates of racemate I[9] (rich in IB), racemate II (rich in IIA), and racemate IV (rich in IVA) were prepared and decomposed to produce mixtures of olefins, the compositions of which are summarized in Table I. The methods of analysis of the olefins are indicated in the footnotes of Table I and in the experimental section.

It is clear from these results that each reaction produced three products. The xanthates of the isomers of 3-phenyl-2-butanol each gave *cis*- and *trans*-2-phenyl-2-butene and 3-phenyl-1-butene. The presence of the last compound in the olefinic products was demonstrated in each case by the optical activity of the mixtures, and by the preparation and isolation of the racemic crystalline 2,4-dinitrobenzenesulfenyl chloride addition compound of this olefin. The production of this olefin from the two xanthates is to be expected, since a hydrogen can be lost from either carbon atom 1 or carbon atom 3 of the xanthate. The estimated amount of 3-phenyl-1-butene present in the mixture came to 30–40% in each case.

The relative amounts of *cis* and *trans* isomers obtained from the two xanthates indicate that the Chugaev reaction proceeds for the most part but not completely in a stereospecific manner. Thus 36% of the purified olefin mixture obtained from the xanthate of I proved to be *cis*-2-phenyl-2-butene, whereas 11–14% of the *trans* isomer was found. From the xanthate of II was obtained hydrocarbon of which 49–52% proved to be *trans*-2-phenyl-2-butene and only a trace of the *cis* isomer was detected. There is no way of determining the stereochemistry of the re-

(9) The numbering system has been maintained throughout papers I, II, III and IV of this series.

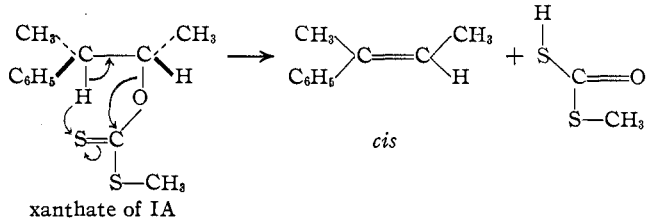
TABLE I

PRODUCTS OF THE CHUGAEV REACTION

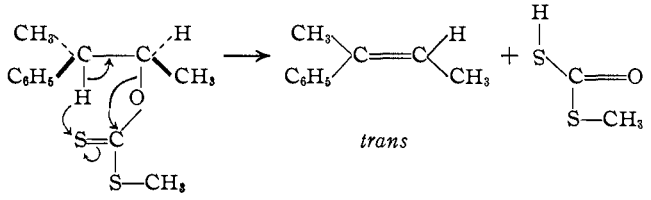
Compos., start. alc., %		Yields, % Xanthate	Tot.[b] olef.	Compn. of olef. mix., [c] % Cis isom.	Trans. isom.	Struct. isom.	Obs. rot., [d] deg. Olef. fract.	Ald. mix.
80	IB				11[e]	40[f]		
20	IA	80	76	36	11[g]	37[h]	−2.02	+75.80
72	IIA				52[e]	32[f]		
28	IIB	85	91	5	49[g]	35[h]	+1.10	−24.78
68	IVA				52[e]	42[f]		
32	IVB	75	67	6	40[g]	55[h]	+6.01	−26.51

[a] The relative amounts of each isomer were estimated from the rotation of the mixture. [b] This yield is based in each case on the sum of the olefin fractions obtained by fractional distillation. [c] Sum of the fractions obtained by fractional distillation = 100%. [d] l = 1 dm. [e] The mixture of the *trans* isomer and the structural isomer (the olefin whose double bond is not in conjugation with the benzene ring) were never separated. Estimates of the amounts of *trans* isomer obtained were made from the amounts of acetophenone isolated from the ozonolysis mixtures (these values were corrected for the small manipulative losses found in a control experiment involving the separation of acetophenone from 2-phenylpropionaldehyde, the other ozonolysis product). [f] These values were obtained by difference, utilizing the estimates of the amounts of the *trans* olefin which were based on the isolation of acetophenone. [g] This estimate is based on the molar extinction coefficients of the spectrum of this mixture (see Fig. 1) at λ = max. The absorption of the olefin whose double bond is not in conjugation with the benzene ring is negligible in this region. A pure sample of 3-phenyl-1-butene was never obtained; however, the spectrum of this substance should simulate that of toluene, which exhibits very weak absorption ($\epsilon > 50$) in the region of 230–240 mμ and should not interfere (see Jones, *Chem. Revs.*, **32**, 1 (1943), and Braude, *et al.*, *J. Chem. Soc.*, 1087 (1947), and Murry, *et al.*, THIS JOURNAL, **70**, 3867 (1948)). [h] These values were obtained by difference, using the estimates of the amounts of *trans* olefin in the mixture, which estimates were based on spectral data.

The Chugaev reaction is considered in the present investigation to go predominantly by the following mechanism. The elimination reaction

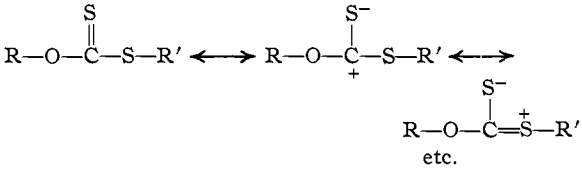


xanthate of IA



xanthate of IIA

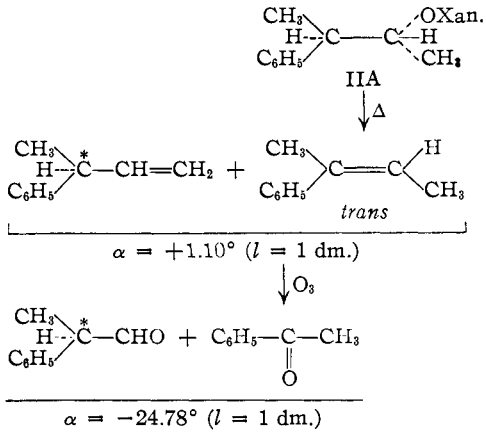
is pictured as being completely concerted, the hydrogen–carbon and the carbon–oxygen bonds breaking at the same time. The decomposition of the thiomethyl carbonate product is considered to be a second and independent reaction, the course of which is not pertinent. The above mechanism differs from that of Stevens and Richmond[2] only insofar as the reaction is thought to be completely concerted, rather than as taking

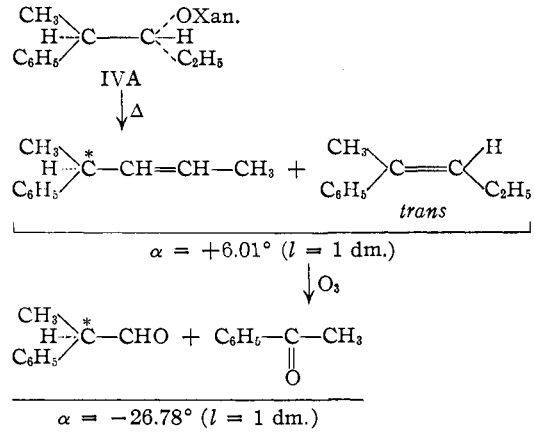


place in steps. This picture of the reaction is preferred over that of Hückel's[3] because the resonance inherent in the xanthate group would tend to increase the nucleophilic character of the sulfur of the thiocarbonyl group over that of the sulfide group. Furthermore, the steric requirements for the attack of the thiocarbonyl group on the hydrogen are less than those of the sulfur bearing a methyl group. The small amount of olefin that arises as a result of a *trans* elimination reaction is considered to be produced by an independent intermolecular mechanism.

The preparation and decomposition of the xanthate of IV (rich in IVA) was carried out for purposes of establishing the configuration of IVA relative to that of the I and II series of alcohols. Production of a large predominance of the *trans* (40–52%) over that of *cis* product (6%) is proof that IV possesses a configuration analogous to that of II.[10] Furthermore, the ozonolysis experiments, the results of which are outlined below, establish that IVA possesses a configuration analogous to IIA. The use of starting materials containing considerable amounts of the corresponding enantiomorphs (IIB and IVB, respectively) in no way modifies the argument. The opposite directions of the rotations of the olefin mixtures obtained from IIA and IB as well as of their respective ozonolysis products (see Table I) confirms the configurational assignments given to these isomeric alcohols in paper I[1] of this series, which were made on the basis of the simple inversion of the *p*-toluenesulfonate of IA by acetate ion to produce the acetate of IIA. The above experiment has demonstrated that the configurations about carbon atom 3 of IB and IIA are enantiomorphically related, and hence the configurations about that carbon atom in IA and IIB must be similarly related, in conformity with the previous argument.

Enough evidence is now available to place the configurational relationships of the four stereoisomers of 3-phenyl-2-butanol and the eight isomers of 2-phenyl-3-pentanol and 3-phenyl-2-pentanol on a secure basis. The configurations of I and II have been established through re-





(10) In making the estimate based on spectral data of the amount of *trans*-2-phenyl-2-pentene obtained from the xanthate of IV (see Table I), the assumption has been made that the spectrum of this substance should be very similar to that of *trans* 2-phenyl-2-butene. The positions of $\lambda_{max.}$ for the curve of the latter compound and the curve of the mixture of *trans* 2-phenyl-2-pentane and 4-phenyl-2-pentene (see Fig. 1) would tend to make this assumption valid.

arrangement studies and through the Chugaev reaction. If one assumes an absolute configuration for IA (this is the only assumption that has to be made), the structures of IB, IIA and IIB become fixed. The structure of IV was related to that of II through the Chugaev reaction, and the configurations of IVA and IIA related to one another by the degradative experiments, thereby fixing the structure of IVB. The *p*-toluenesulfonate of IVA was rearranged (acetolysis) in a stereospecific and predictable fashion to give acetate VIA, thereby fixing the structures of VIA and VIB. The structure of VIA was related to that of VA through simple inversion of the *p*-toluensulfonate of VIA by acetate ion to give acetate of VA, thereby fixing the structure of VA and VB. The *p*-toluenesulfonate of VA upon acetolysis produced IIIB acetate in a stereospecific and predictable manner thereby fixing the structure of IIIA and IIIB. Thus the assignments of configuration made earlier in the work and based for the most part on analogies between physical properties have been substantiated through the use of chemical introconversions and degradative experiments.

The olefinic products of the acetolysis of the *p*-toluenesulfonates of IA and IIA reported in paper I of this series were identified through the preparation of their addition compounds with 2,4-dinitrobenzenesulfenyl chloride. In each case the product obtained proved to be the derivative of *cis*-2-phenyl-2-butene. This fact suggests that the olefin arises from a non-asymmetric intermediate, possibly a free carbonium ion. Such an ion could be formed while the relative rotational positions of the two asymmetric carbon atoms with respect to each other was not conducive to the ring closure that leads to the acetate product.

Experimental

Preparation of *cis*- and *trans*-2-Phenyl-2-butene.—Methylethylphenylcarbinol (260 g.) was prepared according to the method of Klages,[11] and this material was held at reflux temperature mixed with 750 ml. of 4 *N* sulfuric acid. The olefin produced was isolated and distilled in the usual manner; weight 208 g., b. p. 80–84° (18 mm.), $n^{25}D$ 1.5347. This material was submitted to fractionation on a center rod column (55 theoretical plates at the highest operating efficiency) at 29.5 mm. of pressure and three fractions were taken: 1st, wt. 52 g., b. p. 82–88°; 2nd, wt. 85 g., b. p. 88–93.8°; 3rd, wt. 48 g., b. p. 93.8–94.0°. The second fraction was submitted to the same procedure to give 25 g. of material boiling below 93.8° and 58 g., b. p. 93.8–94.0°. All the fractions boiling below 88° were combined and treated by the same procedure to produce 22 g. of olefin, b. p. 77–78°, 45 g., b. p. 78–83°, and 30 g., b. p. 83–94°. Several refractionations of the middle boiling portions finally produced a total of 33 g. of material, b. p. 77–78°, and 128 g. of material, b. p. 93.8–94°. Careful redistillation of the higher boiling olefin gave 124 g. of pure *cis* isomer, b. p. 93.9–94.0° (p = 29.5 mm.), b. p. 194° (p = 1 atm.), $n^{25}D$ 1.5393, d^{25}_4 0.9799, MR_D 45.08, $\lambda_{max.}$ 243 mμ, log ε 4.082. The physical properties of this substance were unaltered by distillation at atmospheric pressure.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.84; H, 9.15. Found: C, 90.92; H, 9.39.

Careful redistillation of the lower boiling olefin produced 29 g. of pure *trans* isomer, b. p. 77.0–77.1° (p = 29.5 mm.), b. p. 174° (p = 1 atm.), $n^{25}D$ 1.5192, d^{25}_4 0.9191, MR_D 45.01, $\lambda_{max.}$ 235 mμ, log ε 3.912. The physical properties of this substance were unchanged by distillation at atmospheric pressure.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.84; H, 9.15. Found: C, 90.72; H, 9.18.

The *cis* isomer (13.5 g.) was mixed with 0.10 g. of pure toluenesulfonic acid and the mixture submitted to slow fractionation at 29.5 mm. to produce 11.4 g. of *trans* isomer, b. p. 77–79° (slight fluctuation), $n^{25}D$ 1.5197.

Equilibration of *cis* and *trans* 2-Phenyl-2-butene.—Pure *cis* isomer (5.0 g.) was heated to 100° with 0.05 g. of *p*-toluenesulfonic acid for three hours, the mixture cooled, shaken with a mixture of petroleum ether and water. The organic layer was washed with alkali, with water, dried, evaporated and distilled; wt. 4.1 g., $n^{25}D$ 1.5334.

Pure *trans* isomer (5.0 g.) when submitted to the same procedure gave 3.6 g. of product, $n^{25}D$ 1.5320.

2,4-Dinitrobenzenesulfenyl Chloride Addition Compounds of *cis*- and *trans*-2-Phenyl-2-butene.—A mixture of 0.50 g. of *cis*-2-phenyl-2-butene, 0.875 g. of 2,4-dinitrobenzenesulfenyl chloride and 2 ml. of glacial acetic acid was stirred until homogeneous and allowed to stand overnight. The heavy prisms that separated were recrystallized from a small amount of glacial acetic acid and petroleum ether; wt., 0.94 g., m. p. 81–82° (rich yellow prisms),[12] mixed m. p. with 2,4-dinitrobenzenesulfenyl chloride, 55–76°.

Anal. Calcd. for $C_{16}H_{15}SN_2O_4Cl$: C, 52.38; H, 4.12. Found: C, 52.27; H, 4.37.

Using the procedure described above, 0.50 g. of *trans*-2-phenyl-2-butene was converted into its addition compound with 2,4-dinitrobenzenesulfenyl chloride to give 0.97 g. of yellow rectangular plates (material recrystallized from ethyl acetate and petroleum ether), m. p. 94–95°, mixed m. p. with same derivative of the *cis* isomer, 59–73°, mixed m. p. with 2,4-dinitrobenzenesulfenyl chloride, 61–81°.

Anal. Calcd. for $C_{16}H_{15}SN_2O_4Cl$: C, 52.38; H, 4.12. Found: C, 52.21; H, 4.12.

Ozonolysis of *cis*- and *trans*-2-Phenyl-2-butene.—Ozone was passed into a mixture of 0.50 g. of *cis* isomer and 10 ml. of ethyl acetate at 0° until no more ozone was absorbed (twenty minutes). The resulting solution was added dropwise to a stirred boiling mixture of 50 ml. of water, 1.0 g. of zinc dust, a trace of silver nitrate and a trace of hydroquinone. After the addition was complete the mixture was cooled and extracted three times with ether, the combined extracts were washed with water, dried and evaporated to an oil, and the oil distilled to give 350 mg. of acetophenone, b. p. (micro) 202.5°. A small sample was converted to the oxime, m. p. 57–58°, mixture m. p. with an authentic sample 58–59°. Another sample was converted to the 2,4-dinitrophenylhydrazone, m. p. 248–249°, mixed m. p. with an authentic sample 248–249°.

From 0.50 g. of the *trans* isomer was obtained by the same procedure 310 mg. of acetophenone, b. p. (micro) 202°. Oxime was prepared from this material, m. p. 57–58°, mixed m. p. with an authentic sample, 58–59°. The 2,4-dinitrophenylhydrazone melted at 248–249°, mixed m. p. with an authentic sample, 248–249°.

Xanthates of I (rich in IB), II (rich in IIA) and IV (rich in IVA).—A mixture of 14.8 g. of II rich in IIA ($[\alpha]^{25}D$ +0.29), 3.85 g. of potassium and 60 ml. of dry toluene were heated at reflux for sixteen hours, cooled and the

(11) Klages, *Ber.*, **35**, 3507 (1902).

(12) The melting point of this substance is sensitive to the rate of heating of the melting point bath; the substance melts at 81–82° if the rate of increase is normal, at 85–86° if very slow. If the substance is recrystallized from ethyl acetate and petroleum ether, the melting point decreases. Material recrystallized after having been melted shows the same characteristics.

small lump of potassium removed with a wire. A large excess (20 ml.) of carbon disulfide was added and the resulting mixture stirred at reflux temperature overnight. The mixture was again cooled and 12 ml. of methyl iodide added, the mixture was held at reflux temperature for four hours, cooled and shaken with a mixture of ether and water. The organic layer was washed with water, dried and the solvent evaporated to a low volume on a steam-bath, and the resulting concentrated solution was submitted to distillation at 15 mm. to remove the toluene. The remaining oil was distilled to give 20.2 g. of xanthate (yellow oil), b. p. 134–135° (p = 3 mm.), $n^{25}D$ 1.5746.

Anal. Calcd. for $C_{12}H_{16}OS_2$: C, 59.96; H, 6.71. Found: C, 60.23; H, 6.83.

The xanthate of I (rich in IB) was prepared by the procedure described above. From 22.0 g. of I rich in IB ($[\alpha]^{25}D$ −18.9°) was obtained 28.8 g. of yellow oil, b. p. 122–123° (p = 1 mm.), $n^{25}D$ 1.5749.

Anal. Calcd. for $C_{12}H_{16}OS_2$: C, 59.96; H, 6.71. Found: C, 60.18; H, 6.81.

The same procedure was used for the preparation of the xanthate of IV (rich in IVA). From 9.5 g. of IV (rich in IVA) ($[\alpha]^{25}D$ −2.64°) was obtained 11.0 g. of xanthate (yellow oil), b. p. 131–132° (p = 2 mm.), $n^{25}D$ 1.5680.

Anal. Calcd. for $C_{13}H_{18}OS_2$: C, 61.37; H, 7.13. Found: C, 61.73; H, 7.45.

Decomposition of the Xanthate of I.—The xanthate of I (rich in IB) (28.8 g.) was heated at 180° in a Wood's metal bath, and the olefin formed was collected as it distilled from the mixture, wt. 16.9 g. of crude yellow material. This material was distilled at reduced pressure (20 mm.) to get rid of low boiling impurities and undecomposed xanthate, wt. 13.7 g. Fractional distillation of this mixture of olefins through a center rod column (55 theoretical plates at the highest operating efficiency) at 29.5 mm. gave three fractions: fraction A, wt. 6.12 g., $n^{25}D$ 1.5093, d^{25}_4 0.8841, MR_D 44.67, b. p. 79.5–80.5°, α −2.01 (l = 1 dm., λ = D); fraction B, wt. 1.55 g., b. p. 80.5–93.8°; and fraction C, wt. 4.32 g., b. p. 93.8–94.0°, $n^{25}D$ 1.5387. Fraction A was analyzed, and Fig. 1 records the ultraviolet absorption spectrum of this mixture.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.84; H, 9.15. Found: C, 90.82; H, 9.38.

Fraction A (1.40 g.) was submitted to ozonolysis (the procedure described earlier for the ozonolysis of *cis*-2-phenyl-2-butene was employed) to produce 0.91 g. of a mixture of acetophenone and 2-phenylpropionaldehyde, α +75.80° (l = 1 dm., λ = D). This mixture (0.50 g.) was dissolved in 5 ml. of ethyl alcohol and added to a suspension of silver oxide in 10 ml. of water (this reagent was prepared just before use by dissolving 1.5 g. of silver nitrate in 10 ml. of water and adding a dilute alkaline solution until no more precipitate formed). The resulting mixture was heated at reflux temperature for half-an-hour, cooled and extracted three times with ether, the extracts were combined, washed with dilute alkaline solution and then with water, dried, evaporated to an oil, and the oil was distilled to give 90 mg. of acetophenone, b. p. (micro) 200°. The 2,4-dinitrophenylhydrazone was prepared, m. p. 248–249°, mixed m. p. with an authentic sample 248–249°.

A known mixture of 250 mg. of acetophenone and 250 mg. 2-phenylpropionaldehyde[1] was submitted to the procedure described above and 230 mg. of acetophenone was obtained, b. p. (micro) 201°, m. p. of the 2,4-dinitrophenylhydrazone, 248–249°, mixed m. p. with an authentic sample, 248–249°.

A mixture of fraction A (325 mg.), 560 mg. of 2,4-dinitrobenzenesulfenyl chloride and 1 ml. of glacial acetic acid was allowed to stand overnight and the resulting oil was dissolved in 3 ml. of benzene and submitted to chromatographic absorption on a small alumina column. The first band to filter through (benzene was used to develop the column) was collected, evaporated under reduced pressure and crystallized and recrystallized from ethyl acetate and petroleum ether to give 110 mg. of optically inactive yellow needles, m. p. 123–124°, depressed by admixture with the 2,4-dinitrobenzenesulfenyl chloride addition products of either *cis*- or *trans*-2-phenyl-2-butene. No other crystalline products could be isolated.

Anal. Calcd. for $C_{16}H_{15}SN_2O_4Cl$: C, 52.38; H, 4.12. Found: C, 52.59; H, 4.39.

Fraction B from the original distillation was discarded. Fraction C (200 mg.) was mixed with 350 mg. of 2,4-dinitrobenzenesulfenyl chloride and 0.5 ml. of glacial acetic acid. The addition compound was isolated and purified in the usual manner; wt. 330 mg., m. p. 81–82°, mixed m. p. with the authentic derivative of *cis*-2-phenyl-2-butene, 81–82°.

Decomposition of the Xanthate of II.—The xanthate of II (rich in IIA) (20.2 g.) was decomposed by the procedure described above to give 12.89 g. of crude olefin, distillation of which produced 11.2 g. of material which was submitted to fractional distillation at 29.5 mm. to give two fractions: fraction A, wt. 8.72 g., b. p. 79–80°, $n^{25}D$ 1.5120, d^{25}_4 0.8831, MR_D 44.92, α +1.10° (l = 1 dm., λ = D); and fraction B, wt. 1.54 g., b. p. 80–84°. Fraction A was analyzed, and Fig. 1 records its ultraviolet absorption spectrum.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.84; H, 9.15. Found: C, 90.42; H, 9.30.

Fraction A (500 mg.) was treated with 2,4-dinitrobenzenesulfenyl chloride in the usual manner and 350 mg. of recrystallized derivative was obtained, m. p. 94–95°, mixed m. p. with an authentic sample of the addition product of 2,4-dinitrobenzenesulfenyl chloride with *trans*-2-phenyl-2-butene, 94–95°. The filtrates from the crystallization and recrystallization of the above substance were concentrated, dissolved in a small amount of benzene, and submitted to chromatographic absorption on a small column of alumina. The column was developed with benzene and the first band to filter through the column was collected, concentrated and the resulting oil crystallized and recrystallized from ethyl acetate and petroleum ether to give 20 mg. of yellow needles, m. p. 124–125°, not depressed by admixture with the corresponding derivative prepared from fraction A obtained from the decomposition of the xanthate of I.

Fraction A (4.4 g.) was submitted to ozonolysis to give 2.7 g. of a mixture of acetophenone and 2-phenylpropionaldehyde, α −24.78° (l = 1 dm., λ = D). This mixture (500 mg.) was oxidized with silver oxide, and the acetophenone was isolated in the usual manner (see above), wt. 302 mg., b. p. 202° (micro), m. p. of the 2,4-dinitrophenylhydrazone, 248–249°.

Fraction B was submitted to fractional distillation, and the material that boiled above 85° (p = 29.5 mm.) and the material held in the column at the end were combined (total wt., 450 mg.) and converted to the 2,4-dinitrobenzenesulfenyl chloride addition product, wt. 640 mg., m. p. 81–82°, not depressed by admixture with an authentic sample of the addition product of 2,4-dinitrobenzenesulfenyl chloride with *cis*-2-phenyl-2-butene.

Decomposition of the Xanthate of IV.—The xanthate of IV (rich in IVA) (10.5 g.) when pyrolyzed at 200° gave crude olefin (5.9 g.) which on distillation produced 4.7 g. of material. This mixture was submitted to fractional distillation at 29.5 mm. and two fractions were taken: fraction A, wt. 3.8 g., b. p. 94.4–98.0°, α +6.01 (l = 1 dm., λ = D); and fraction B, wt. 0.23 g., b. p. 98–101°. Fraction A was analyzed, and Fig. 1 records its ultraviolet absorption spectrum.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.18; H, 9.91.

Fraction A (1.5 g.) was submitted to ozonolysis to produce 0.83 g. of a mixture of acetophenone and 2-phenylpropionaldehyde, α −26.51° (l = 1 dm., λ = D). This mixture (500 mg.) was oxidized with silver oxide by the procedure reported above and 240 mg. of acetophenone was isolated, b. p. 201° (micro). The 2,4-dinitrophenylhydrazone of this substance melted at 248–249°, not depressed by admixture with an authentic sample.

Identification of Olefin from Rearrangement Studies.—The olefin (0.55 g.) obtained from the acetolysis of the *p*-toluenesulfonate of IA (see paper I of this series) was treated in the usual manner with 2,4-dinitrobenzenesulfenyl chloride, and 0.65 g. of recrystallized product obtained, m. p. 81–82°, not depressed by admixture with the same derivative of an authentic sample of *cis*-2-phenyl-2-butene.

In the same way the olefin (0.12 g.) obtained from the acetolysis of the *p*-toluenesulfonate of IIA (see paper I of this series) was converted to the 2,4-dinitrobenzenesulfenyl chloride addition compound, wt. 90 mg. (recrystallized material), m. p. 81–82°, not depressed by admixture with an authentic sample of the same derivative of *cis*-2-phenyl-2-butene.

Acknowledgments.—The author wishes to thank Welton Burney for the analyses reported in this paper. The use of the reagent, 2,4-dinitrobenzenesulfenyl chloride was made possible through the kindness of N. Kharasch, who provided a sample of the substance and directions for its use, and who also made information available as to the direction of addition of the reagent to the carbon–carbon double bond.

Summary

1. The geometric isomers of 2-phenyl-2-butene have been prepared, configurational assignments have been made on the basis of physical properties, and solid derivatives have been prepared.

2. Evidence has been adduced for the stereospecific addition of 2,4-dinitrobenzenesulfenyl chloride to the carbon–carbon double bond.

3. The Chugaev reaction has been shown to be predominantly a *cis* elimination reaction in an acyclic system.

4. Evidence has been obtained for the relative configurations of all the stereoisomers of 3-phenyl-2-butanol, 2-phenyl-3-pentanol and 3-phenyl-2-pentanol.

5. The formation of olefin during the acetolysis of the *p*-toluenesulfonates of IA and IIA has been shown to be a non-stereospecific reaction.

LOS ANGELES, CALIFORNIA RECEIVED MARCH 14, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of Phellandral[1,2]

BY ROBERT L. FRANK, ROBERT E. BERRY AND ODETTE L. SHOTWELL

Most of the evidence concerning the structure of the terpene phellandral has indicated that this naturally occurring aldehyde is best represented by Structure X.[3,4,5] Cooke, Macbeth and Swanson[5b] have established the structure of the carbon skeleton by hydrogenation of phellandric acid to the known *cis*- and *trans*-hexahydrocuminic acids, and ultraviolet absorption spectra have located the double bond in the position α,β to the carbonyl group.[5a,6] This structure has now been confirmed by the synthesis of *dl*-phellandral through *dl*-phellandric acid, and the resolution of the racemic acid to the *d*-form corresponding to the acid obtained by oxidation of *d*-phellandral. The steps to the aldehyde are represented by Structures I–X.

The starting material, *p*-isopropylphenol (I), was best prepared by sulfonation of cumene, followed by alkali fusion. Methods involving nitration, reduction and diazotization or the alkylation of phenol resulted in mixtures of *o*- and *p*-isopropylphenols.

The hydrogenation and oxidation steps (I–II–III) were straightforward and gave yields of 96 and 82%, respectively.

In the preparation of the cyanohydrin acetate of 4-isopropylcyclohexanone (V) it was expected that treatment of the ketone with acetic anhydride and aqueous potassium cyanide[7] would lead directly to the cyanohydrin acetate. The reaction was tried on cyclohexanone as a model compound, and it was found to yield not the acetate but the cyanohydrin itself. The latter is resistant to acetylation by acetic anhydride, giving only 19% acetylation even in an excess of the reagent. Subsequent experiments showed that if one adds a trace of acetyl chloride to the acetic anhydride, the acetylation proceeds smoothly in good yields (64% with cyclohexanone). The conversion of 4-isopropylcyclohexanone (III) to the cyanohydrin acetate (V) was then carried out in two stages, but without purification of the intermediate cyanohydrin (IV), in a yield of 70%.

The method of Burns, Jones and Ritchie[8] and others[9] for the pyrolysis of esters gave excellent results with 4-isopropylcyclohexanone cyanohydrin acetate (V). The optimum temperature for our ester was 575–600°, which resulted in a small amount of charring in the pyrolysis tube, but nevertheless gave the highest yields (74%) of 4-isopropyl-1-cyano-1-cyclo-

(1) Presented in part at the St. Louis meeting of the American Chemical Society, 1948, before the Division of Organic Chemistry.

(2) This is the second communication on the chemistry of terpenes. For the first, see THIS JOURNAL, **71**, 1387 (1949).

(3) Schimmel's Report, 1904, Oct., p. 88; Simonsen, "The Terpenes," Cambridge University Press, 2nd edition, 1947, Vol. I, p. 308.

(4) Wallach, *Ann.*, **340**, 13 (1905); **343**, 33 (1905).

(5) (a) Cooke and Macbeth, *J. Chem. Soc.*, 1408 (1938); (b) Cooke, Macbeth and Swanson, *ibid.*, 808 (1940); (c) Burger and Macbeth, *ibid.*, 145 (1946).

(6) Evans and Gillam, *ibid.*, 565 (1943).

(7) Snyder, Stewart and Myers, THIS JOURNAL, **71**, 1055 (1949).

(8) Burns, Jones and Ritchie, *J. Chem. Soc.*, 400 (1935).

(9) (a) Schniepp and Geller, THIS JOURNAL, **67**, 54 (1945); (b) Ratchford and Fisher, *ibid.*, **69**, 1911 (1947).