

Countercurrent distribution in a 50-tube Craig machine, using the system chloroform against 0.2 *M* aqueous phosphate buffer (*pH* 7.53), gave, for each sample, a single peak at tube 34. The shape of the peak for each sample corresponded with the theoretical curve for a single component

peaking at tube 34. The ultraviolet absorption spectra of both peak tube contents were identical with each other and with those of the two starting materials.

PEARL RIVER, NEW YORK

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

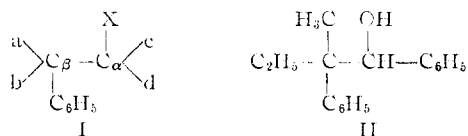
Studies in Stereochemistry. XXVI. Solvolytic Rearrangements in the 1,2-Diphenyl-2-methyl-1-butanol System¹

BY DONALD J. CRAM AND JANET ALLINGER

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The tosylates of the optically pure diastereomers of the 1,2-diphenyl-2-methyl-1-butanol system have been solvolyzed in dry acetic and formic acids, respectively. Phenyl migration from *C*_β dominates the reaction course, at the most only a trace of alkyl migration being observed. In the more nucleophilic and poorer ionizing solvent (acetic acid), a larger amount of unrearranged product was observed, the simple substitution reaction being somewhat stereospecific in the *direction of inversion*. In the less nucleophilic and better ionizing solvent (formic acid), a smaller amount of unrearranged product was observed, the simple substitution reaction being somewhat stereospecific in the *direction of retention*. The results indicate that three stereochemically discrete processes compete with one another, all three leading to simple substitution product: (1) a simple solvolytic inversion mechanism; (2) a simple solvolytic mechanism whose specificity is sterically induced by the asymmetry at *C*_β; (3) a phenonium ion mechanism which can lead to simple substitution product with retention of configuration. That rearranged products arise from both bridged and rearranged open carbonium ions is indicated.

In previous investigations of this series, the solvolytic behavior of systems I have been studied in which *a* = *c* = alkyl and *b* = *d* = hydrogen²; *a* = *b* = *c* = *d* = alkyl³; *a* = alkyl, *b* = *c* = hydrogen and *d* = phenyl⁴; and *a* = phenyl, *b* = *c* = hydrogen and *d* = alkyl.⁵ Others have studied systems I in which *a* = alkyl, *b* = *c* = *d* = hydrogen⁶; *a* = *b* = *c* = hydrogen and *d* = alkyl⁷; *a* = *c* = phenyl, *b* = *d* = hydrogen.⁸ The tendency for phenyl to participate in ionization was found to vary markedly with the electrical nature of substituents at *C*_α and *C*_β, as well as the character of the solvent, and the steric situation within the molecule. The 1,2-diphenyl-2-methyl-1-butanol



system (II) belongs in a borderline category with respect to phenyl involvement in ionization, and this paper reports the results of an investigation of the acetolysis and formolysis of its diastereomeric tosylates.

Methods

The four stereoisomers of II were isolated in a pure state and their configurations assigned in a previous investigation.⁹ The four tosylate deriva-

(1) This work was sponsored by the Office of Ordnance Research, U. S. Army.

(2) (a) D. J. Cram, *THIS JOURNAL*, **71**, 3863 (1949); (b) **71**, 3875 (1949); (c) **74**, 2129 (1952); (d) **74**, 2159 (1952); (e) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (f) D. J. Cram, *ibid.*, **75**, 332 (1953).

(3) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).

(4) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 339 (1953).

(5) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **76**, 28 (1954).

(6) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

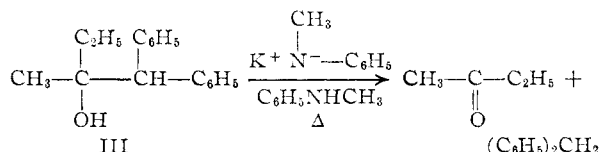
(7) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952).

(8) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955).

(9) D. J. Cram and J. Allinger, *ibid.*, **76**, 4516 (1954). The meaning of the configurational terms *threo* and *erythro* as applied to system II are defined in this reference.

tives were prepared from the corresponding potassium alcoholates and tosyl chloride, the derivatives possessing the *threo* configuration being particularly unstable. The products were isolated in the usual way, the olefin-ester mixtures being converted (LiAlH_4) to alcohol-olefin mixtures which were separated into olefin and alcohol components. In runs involving *erythro* materials and *threo* materials, 73 and 87%, respectively, of the starting materials were accountable.

Analysis of Alcohol Fractions.—Comparison of the infrared spectra of the alcohol components obtained from the solvolyses with those of *threo*- and *erythro*-II and of III (product of phenyl migration) suggested the bulk of the material to consist of these components. Accordingly, infrared analytical procedures were developed based on these three components utilizing the six most advantageous wave lengths in the infrared for analysis. Two independent sets of three simultaneous equations when solved provided estimates of percentage composition. Known mixtures of the three components indicated the deviations from Beer's law to be small. The analyses for the acetolysis runs (runs 1 and 2 of Table I) for the total secondary alcohol (diastereomers of II) and ter-



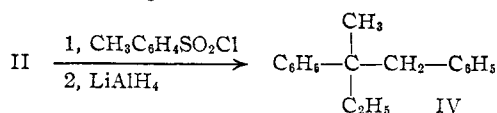
tiary alcohol III have a probable error of about 2% since the optical densities differ by factors from 1 to 4. The analyses for the individual diastereomers of II are grossly inaccurate because the optical densities of these components are rather close together, the biggest factor being 1.6. To improve the accuracy of this analysis and to examine the optical character of the diastereomeric components (II), the alcohol mixtures were heated with strong

TABLE I
ESTIMATED %-COMPOSITION OF ALCOHOL PRODUCTS FROM THE SOLVOLYSES OF TOSYLATE ESTERS OF 1,2-DIPHENYL-2-METHYL-2-BUTANOL (II)

Run	Solvent	Config. st. mat.	Infrared analysis ^a					
			At 1355, 1054 and 895 cm. ⁻¹ % III	% threo-II	% erythro-II	At 1245, 1145 and 885 cm. ⁻¹ % III	% threo-II	% erythro-II
1	AcOH	(+)-threo-II	19	22	64	21	17	63
2	AcOH	(+)-erythro-II	24	32	45	29	25	46
3	HCOOH	(-)-threo-II	65	15	23
4	HCOOH	(-)-erythro-II	70	6	26
	Known mixture ^b		29	32	39	32	34	37
	Known mixture ^c		45	24	35	51	17	36
			At 1054 and 895 cm. ⁻¹		At 916 and 885 cm. ⁻¹		Polarimetric analysis	
			% threo	% erythro	% threo	% erythro	% threo-II	% erythro-II
	II from run 1		30	73	28	75	30	70
	II from run 2		47	55	43	62	44	56
	II from run 3		58	45	57	47	54	46
	II from run 4		26	76	27	74	25	75
	Known mixture ^d		58	48	57	50		
	Known mixture ^e		28	75	32	73		

^a Details of the method are in Experimental. ^b 30% III, 36% threo-II, 33% erythro-II. ^c 46% III, 23% threo-II, 31% erythro-II. ^d 54% threo-II, 46% erythro-II. ^e 32% threo-II, 68% erythro-II.

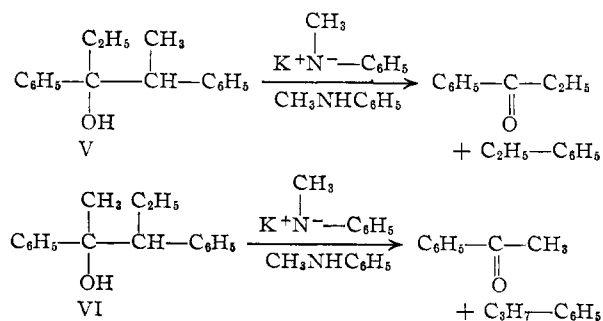
base under conditions that destroyed III and left II.¹⁰ The isolation of diphenylmethane from the reaction provides qualitative evidence for III in the starting material. The diastereomeric mixtures of II thus obtained were submitted to a two-component infrared analysis utilizing four wave lengths in the infrared and appropriate known mixtures. A polarimetric analysis was also used (a plot of rotation *vs.* % composition is linear)⁹ based on the assumption that the diastereomers were optically pure. The agreement between the two methods indicates this assumption to be valid. Independent evidence for their optical purity was found in the coincidence of rotations of IV obtained from known mixtures of optically pure diastereomers and from these mixtures obtained from the acetolyses. Table I records the results of these analyses, a sample of raw data being recorded in the Experimental.



The rotations of alcohols obtained from the acetolysis containing tertiary alcohol III were of course different from the corresponding alcohols after III had been removed. To see if III was active or inactive, synthetic mixtures of optically pure *threo*- and *erythro*-II and racemic III were prepared in the same proportions as the mixtures obtained from the solvolysis reactions. The rotations of these mixtures demonstrated that the rotational contributions of the three components were virtually additive. The differences in rotation between the synthetic mixtures and those obtained from the solvolyses suggest that the tertiary alcohol III in the solvolysis mixtures possesses a specific rotation of about 5° in the presence of *threo*- and *erythro*-II. The large number of analytical values utilized in the calculation makes this conclusion tentative. Since optically pure III was not pre-

pared, the *degree* of optical purity of the III produced from the solvolyses cannot be estimated.

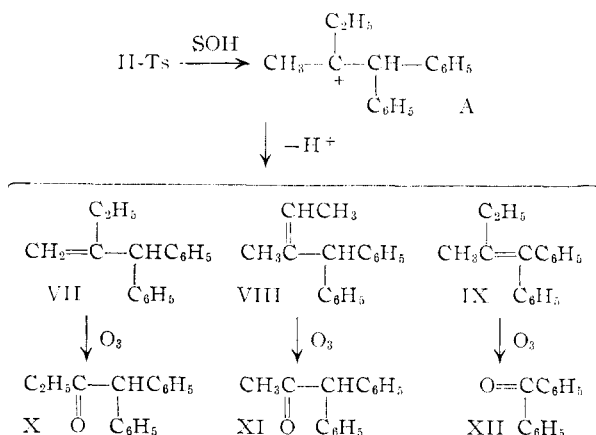
Similar analytical procedures were applied to the formolysis products (runs 3 and 4, Table I). Although the analysis at the first set of wave numbers gave internally consistent data (the sum of the components came to 100%), some of the values at the other set were not real. After being submitted to the treatment with base, the polarimetric and infrared analysis of the alcohol product pointed to the presence of only *threo*- and *erythro*-II in this final mixture. These facts suggest that small amounts of other components were present in the initial alcohol mixtures obtained from solvolysis, which were destroyed by the treatment with base. The ketone fragments obtained from the basic treatment were converted to their 2,4-dinitrophenylhydrazones. Although crystalline derivatives were obtained, pure compounds could not be isolated. The color of the solid material was characteristic of derivatives of ketones conjugated with benzene rings. The data taken as a whole suggest the contaminants to be products of either methyl or ethyl migration (V to VI) or both, which upon treatment with strong base would give acetophenone and propiophenone, respectively.¹⁰ Unfortunately, the trace amounts involved did not permit definitive identification.



Analysis of Olefin Fractions.—Since the starting material (tosylate of II) is incapable of going directly to olefin, only rearranged olefins were

(10) D. J. Cram, J. Allinger and A. Langemann, *Chemistry & Industry*, 919 (1955).

possible products of the reaction. Three olefins VII, VIII and IX could arise from the carbonium ion A produced by phenyl migration during the solvolysis of II-Ts. The analysis problem was simplified by converting the mixture of olefins obtained to their ketones (X, XI and XII) through ozonolysis, the ketonic mixtures being analyzed



through infrared techniques for these three components (see Experimental for details). The 2,4-dinitrophenylhydrazone of XI was isolated from the ketonic mixture obtained in run 2 and was compared with an authentic sample. These analyses provided only estimates of the amounts of the three components, since small amounts of unidentified components ($\sim 10\%$) interfered. Table II records these estimates as well as the yields of olefin and ketone obtained.

TABLE II

ESTIMATED % COMPOSITION OF KETONE DERIVED FROM OLEFINS ARISING IN SOLVOLYSIS OF II-Ts

Run ^a	Yield olefin, %	Compn. ketone mixture, %	X	XI	XII
1	67	14	67	11	
2	55	11	69	11	
3	49	3	68	9	
4	42	8	72	16	

^a Run numbers same as in Table I. ^b Details of method are in Experimental. ^c Based on tosylate.

Control Experiments.—Control experiments demonstrated that the acetates of II and III once formed were stable. The formates of II and III could not be prepared. The stabilities of the diastereomeric 1,2-diphenyl-1-propyl formates in formic acid at 25° have been examined previously⁴ and were found to have been formed decidedly faster than they were interconverted. The similarity between this system and II taken in conjunction with the balance between the diastereomeric formates obtained from formolysis of II-tosylate (see Table I) indicates that the formates are formed somewhat faster than they react. The olefinic products in both the formolysis and acetolysis were demonstrated not to change upon further submission to solvolysis conditions. Earlier results¹¹ suggest that the balance of olefins is kinetically controlled in the acetolysis reaction, but might be thermodynamically controlled in the formolysis.

(11) D. J. Cram, *THIS JOURNAL*, **74**, 2137 (1952).

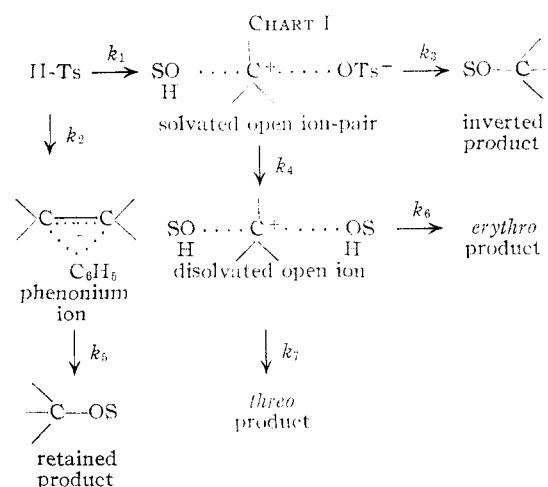
The effectiveness of the removal of III from mixtures of II and III by treatment with strong base was demonstrated with experiments utilizing synthetic mixtures.

Discussion

The Products of Simple Substitution.—The results indicate that in the solvolysis of the 1,2-diphenyl-2-methyl-1-butyl system, a number of primary processes compete with one another, each of which leads to intermediates that partition between several different products. Phenyl and solvent participation in ionization are the likely primary processes, the first leading to phenonium ion,² the second to solvated open ion. Evidence for these two primary processes is found in the stereochemical course of substitution that occurs *without rearrangement*. In acetolysis the ratios of

Starting material	<i>erythro</i> -II-Ac <i>threo</i> -II-Ac	<i>erythro</i> -II-Fm <i>threo</i> -II-Fm
<i>threo</i> -II-Ts	2.3	0.85
<i>erythro</i> -II-Ts	1.3	3.0

erythro to *threo* acetates are different from the diastereomeric starting materials, predominating inversion occurring with *threo* and predominating retention with *erythro* material. These results can be most simply interpreted without assuming a phenonium ion intermediate. In Chart I, the starting material (II-Ts) can ionize with either phenyl or solvent participation, depending on the values of k_1 and k_2 . If $k_1 \gg k_2$, then the balance between product of retained and inverted configuration is controlled by the relative values of k_3 and k_4 on the one hand and k_5 and k_7 on the other. For the acetolysis of *threo*-II-Ts, k_3 being greater than k_4 explains the results. With *erythro*-II-Ts $k_4 > k_3$ and $k_6 > k_7$. Since the disolvated open ion is the same for each diastereomer,¹² k_6 and k_7 should be independent of starting configuration. This predisposition of the system to give *erythro* material is



consistent with previous generalizations.^{2e,13} The over-all process described by k_1 - k_3 is similar in its

(12) Implicit in this statement is the assumption that the disolvated ion has a half-life longer than that of the half-life of the rotations which lead to equilibration between the various conformations.

(13) D. J. Cram and F. A. Abd Elhazef, *THIS JOURNAL*, **74**, 5851 (1952).

steric requirements to SN_2 processes, which is visualized in Chart II as occurring with the displacing group (X^-) coming across the smallest group (S) attached to the adjacent asymmetric carbon atom. The transition state for isomer A which is a model for *threo*-II-Ts should be more stable than that for B which is a model for *erythro*-II-Ts. Thus $k_3 > k_4$ for *threo*-II-Ts and $k_4 > k_3$ for *erythro*-II-Ts. Of the three conformations of the disolvated open ion in Chart III, only C allows the incoming solvent to come in across the smallest

CHART II

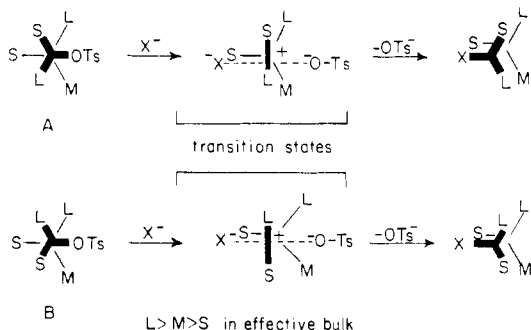
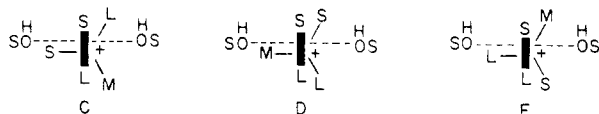
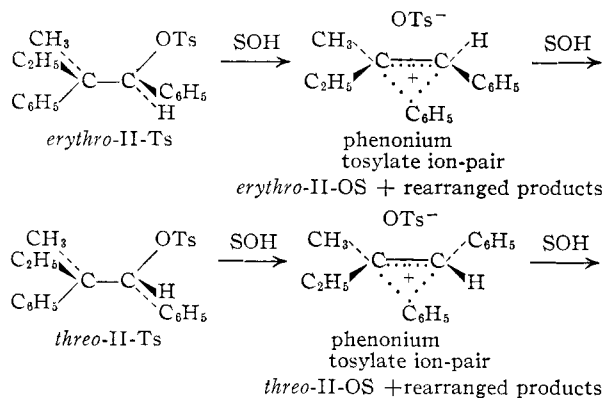


CHART III



group (S) attached to the adjacent carbon, and at the same time allows the two large groups (L) to be as far away from each other as possible. Thus *erythro* product should dominate, and $k_6 > k_7$, as is indeed observed.



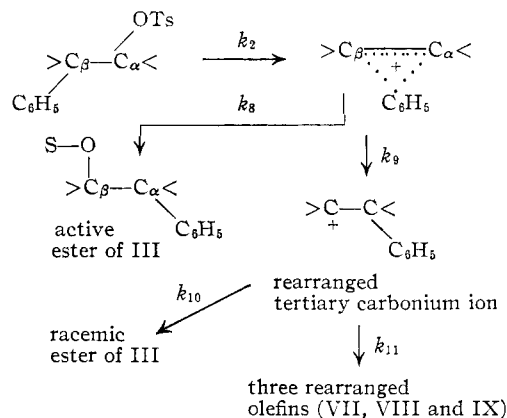
In the formolysis, on the other hand, with both starting materials the simple substitution reactions occurred with predominating retention of configuration. The stereospecificity was more marked with *erythro* isomer as the starting material. In this more ionizing and less nucleophilic solvent, the results cannot be explained only on the basis of the primary process described by k_1 . In view of the facts that much of the product has undergone phenyl rearrangement and that in other systems a phenonium ion intermediate has been demonstrated,² it seems likely that the process described by k_2 leading to a phenonium ion is responsible for

the dominating retention process. That the retention is more marked with *erythro* starting material is probably due to $k_4 > k_3$ in formic acid, and $k_6 > k_7$ (the relative values of these rates should be much more insensitive to solvent).

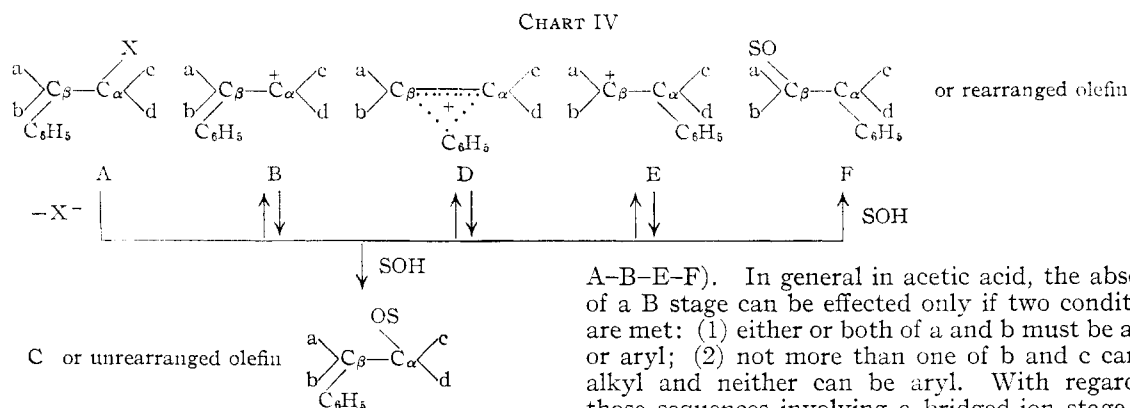
Although other processes such as the formation of phenonium ions from open ions or *vice versa* or ion-pair collapse might also play a role in the solvolyses, they are not demanded by the data.

The Products of Rearrangement.—Although the migration of methyl or ethyl groups probably occurred to a small extent particularly in the formolysis, the reaction products were largely those in which a phenyl migration had occurred. In the acetolysis the ratios of rearranged to unrearranged product were 4.6 and 4.0 for *erythro* and *threo* materials, respectively, while the corresponding values in the formolysis were 6.1 and 5.2. In each solvent, the amount of starting material accounted for was higher (85–88%) with *threo* than with *erythro* starting material (75–71%), and the absolute yields of both rearranged and simple substitution products were greater for the *threo* than for the *erythro* materials. It is clear that neither the slightly more important eclipsing effects expected from the phenonium bridge from *erythro* material nor the greater ease with which *threo* material enters into simple substitution play anything more than minor roles in directing the reaction courses.

The question of the optical purity of the tertiary alcohol III ultimately obtained in these experiments unfortunately was not settled. What few data are available suggest that it was at least partially active, which in turn points to the process de-



scribed by k_2 – k_8 . That most of the tertiary ester came from rearranged open ion (k_2 – k_8) in the acetolysis is suggested by the fact that the ratios of yields of olefin (rearranged) to rearranged tertiary alcohol are about the same from both *threo* and *erythro* starting materials (15.2 and 14.1, respectively). The absolute yields of rearranged alcohol III were much higher (factor of 6) in the formolysis, and the ratios of yields of olefin to alcohol III were 1.71 and 1.61 from *threo* and *erythro* materials. In this solvent probably a lower proportion of III-ester came from rearranged open ion and a higher proportion directly from the phenonium bridge. That bridged ion-pairs go directly to ester product in the more dissociating formic acid solvent (as contrasted to acetic acid) has been demonstrated in other sys-



tems.^{2c,e,14} That essentially all of the olefin came through the rearranged open ion (process k_9 - k_{11}) in acetic acid is indicated by the fact that their ratios are independent of the starting configuration (see Table II). The same thing also probably is true in formic acid, although the analyses were so poor due to contaminants that this has not been demonstrated (Table II). It is interesting that in both solvents only small amounts of the most conjugated olefin (IX) were formed, presumably because of eclipsing effects.

The Variation in Mechanism of the Wagner-Meerwein Rearrangement (Phenyl the Migrating Group) as a Function of the Substituents at C_α and C_β .—Enough systems have now been studied in detail so that the dependency of the mechanism on the non-migrating substituents at C_α and C_β can be examined from a general standpoint. The kinetic tool has been particularly valuable in gaining evidence for participation of neighboring phenyl in ionization in those systems where marked driving forces were evident and were not masked by steric or inductive effects, or by the intervention of internal return¹⁴ (ion-pair collapse).^{2c} In the latter cases and those that are borderline, the use of stereochemical and product-analysis techniques have provided not only evidence for or against the participation of neighboring phenyl in ionization, but also evidence for bridged ionic intermediates, ion-pair collapse, and the partitioning of bridged and open ion intermediates between various paths leading to product. The use of C^{14} as a tracer has also been used advantageously for many of the same purposes.

Chart IV represents a general and simplified mechanistic scheme, reference to which permits the classification of systems according to what stereochemically differentiated gross mechanism for solvolysis applies. The capital letters refer to discrete species and the dashes to transition states separating these species. These data show that by appropriately substituting C_α and C_β and by utilizing the proper solvents, many combinations of intermediates can be detected. The following sequences have not been demonstrated: A-F, A-E-F (as distinct from a possible A-D-E-F), A-B-E-F (as distinct from a possible A-B-D-E-F), A-B-D-F (as distinct from a possible A-B-D-E-F), A-B-D-E-F (as distinct from a possible

A-B-E-F). In general in acetic acid, the absence of a B stage can be effected only if two conditions are met: (1) either or both of a and b must be alkyl or aryl; (2) not more than one of b and c can be alkyl and neither can be aryl. With regard to those sequences involving a bridged-ion stage (D-stage), the bridge opens at the carbon which could lead to the most stable carbonium ion. It is interesting in this connection that the last two systems of Chart IV (a = CH_3 , b = C_2H_5 , c = C_6H_5 , and d = H; a = CH_3 , b = C_2H_5 , c = CH_3 , d = C_2H_5) behaved similarly. In the first of these, the bridge appeared to open in both directions, the quaternary being favored over the benzyl carbon. In the second of these, the bridge of course opened in both directions. In both systems open carbonium ions (B and E stages) appeared to be intermediates.

a — C_β — b		c — C_α — d		Mechanisms ^a
CH_3	H	H	H	A-D-F ^b
C_6H_5	H	H	H	A-D-?-F ^{c,d}
CH_3	CH_3	H	H	A-D-?-F ^{c,d}
C_6H_5	C_6H_5	H	H	A-D-?-F ^{c,d}
H	H	CH_3	H	A-B-C, A-D-C ^e
CH_3	H	CH_3	H	A-D-C, A-D-F ^f
C_2H_5	H	CH_3	H	A-D-C, A-D-F, A-D-E-F ^g
CH_3	H	C_2H_5	H	A-D-C, A-D-F, A-D-E-F ^g
C_2H_5	H	C_2H_5	H	A-D-C, A-D-F ^h
C_6H_5	H	CH_3	H	A-D-E-F, A-D-F ⁱ
CH_3	CH_3	CH_3	H	A-D-?-F ^d
CH_3	H	C_6H_5	H	A-B-C, A-D-C ^j
C_6H_5	H	C_6H_5	H	A-B-C, A-B-E-F or A-B-D-E-F ^k
CH_3	C_2H_5	C_6H_5	H	A-B-C, A-D-C, [*] A-B-D-E-F, ^l A-D-F ^{m,n}
CH_3	C_2H_5	CH_3	C_2H_5	A-B-C, A-D-C, A-B-D-E-F ^{l,n}

^a Only the dominant mechanism is put down except where small amounts of processes involving a D stage were detected. The solvent is acetic acid except those marked with an asterisk, where formic acid was employed. X is tosylate or brosylate, except where indicated differently. ^b S. Winstein and K. C. Schreiber, *THIS JOURNAL*, **74**, 2171 (1952). ^c S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1116 (1952). ^d Kinetic techniques indicated rate enhancements due to phenyl participation in ionization; products were not examined. ^e S. Winstein, M. Brown, K. F. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952). ^f Ref. 2a, 2c. ^g Ref. 2b, 2d. ^h Ref. 2e. ⁱ D. J. Cram and F. A. Abd Elhafez, *ibid.*, **76**, 28 (1954). ^j Ref. 4. ^k Ref. 8. ^l Only probable. ^m Present study. ⁿ Ref. 3. X was a *p*-bromobenzoate group.

Experimental Part

Tosylates of the Four Stereoisomers of 1,2-Diphenyl-2-methyl-1-butanol (II).—The procedure is illustrated with the preparation of the derivative of (+)-*erythro*-II. A mixture of 100 ml. of dry C.P. benzene, 8.95 g. of (+)-*erythro*-II

(14) S. Winstein and K. C. Schreiber, *THIS JOURNAL*, **74**, 2165 (1952).

$[\alpha]^{25}_D +1.86^\circ$ (benzene, c 10.1)⁹ and 1.5 g. of potassium metal were held at reflux under anhydrous conditions under nitrogen for 4 hours. The mixture was cooled to 0° , 7.16 g. of freshly crystallized tosyl chloride was added under nitrogen and the resulting mixture was stirred for 30 minutes. The mixture was filtered always keeping the cake wet with benzene (metallic potassium). The filtrates were washed with water, twice with dilute sodium carbonate solution, again with water and dried. The solvent was evaporated at 25° , and the residue was crystallized from pentane at 0° to give a 6.5-g. 1st crop and a 1.46-g. 2nd crop. Recrystallization of this material from an ether-pentane mixture at 0° afforded 6.4 g. (43% yield) of white needles, m.p. 52° dec., $[\alpha]^{25}_D +60.2^\circ$ (benzene, c 3.91).

Anal. Calcd. for $C_{24}H_{26}SO_3$: C, 73.06; H, 6.64. Found: C, 73.08; H, 6.60.

In a similar manner, 8.7 g. of (-)-*erythro*-II $[\alpha]^{25}_D -1.91^\circ$, (benzene, c 10.5)⁹ was converted to 9.8 g. (69% yield) of tosylate ester, m.p. 54° dec., $[\alpha]^{25}_D -59.8^\circ$ (benzene, c 3.70).

Anal. Calcd. for $C_{24}H_{26}SO_3$: C, 73.06; H, 6.64. Found: C, 73.23; H, 6.51.

Similarly, from (+)-*threo*-II $[\alpha]^{25}_D +59.4^\circ$ (benzene, c 10.4)⁹ was obtained a 74% yield of tosylate (white needles), m.p. 54° dec. This ester was so unstable it decomposed before rotations and analysis could be obtained. From (-)-*threo*-II $[\alpha]^{25}_D -59.3^\circ$ (benzene, c 10.4)⁹ was obtained a 53% yield of tosylate (white needles), m.p. 56° dec. The sample decomposed before rotation could be recorded.

Anal. Calcd. for $C_{24}H_{26}SO_3$: C, 73.06; H, 6.64. Found: C, 73.19; H, 6.90.

Acetolysis of the Tosylates of the Isomeric 1,2-Diphenyl-2-methyl-1-butanols (II).—A solution of 1722 ml. of freshly distilled acetic acid, 64 ml. of acetic anhydride and 12.5 g. of C.P. anhydrous potassium carbonate was heated at reflux for 24 hours and cooled. This solution was 0.1002 M in potassium acetate. The tosylate of (+)-*erythro*-II (6.4 g., run 2) was added to 180 ml. of this solution. Solution of the ester required 20 minutes. This solution protected from moisture was allowed to stand at 25° for 83 hours, and then poured into 600 ml. of water containing 10 ml. of a saturated sodium chloride solution. The resulting mixture was extracted with pure pentane, the pentane solution was washed with water, sodium bicarbonate solution and again with water. The organic layer was dried, evaporated, and the residual oil was distilled at 2 mm. with a final bath temperature of 135° to give 4.21 g. of colorless oil. The small amount of residue (<0.05 g.) when triturated with water gave an acidic solution. The distillate was added to a stirred mixture of 0.4 g. of lithium aluminum hydride and 100 ml. of anhydrous ether and, after stirring for 50 minutes at 25° , the mixture was diluted first with wet ether and then with ice-cold water. The layers were separated, the organic layer was washed with water, dried and evaporated to an oil. This oil was dissolved in 5 ml. of pure pentane and chromatographed on a column of 120 g. of neutral Activity III alumina¹⁵ made up in pentane. The olefin was washed from the column with pentane, 1.98 g. of distilled eluate being obtained, n^{25}_D 1.5690, $\alpha^{25}_D +0.09^\circ$ (1 dm., neat). The alcoholic fraction was eluted with 250 ml. of C.P. methanol to give 0.59 g. of viscous oil (distilled material), n^{25}_D 1.5689, $[\alpha]^{25}_D +24.1^\circ$ (benzene, c 10.0). These two fractions (olefin and alcohol) were used in the subsequent infrared and polarimetric analyses.

A similar acetolysis and isolation procedure (run 1) as applied to the tosylate of (+)-*threo*-II (6.10 g.) gave 3.5 g. of distilled alcohol-olefin product (residue 0.03 g.). Chromatographic separation of these fractions gave 2.33 g. of olefin, n^{25}_D 1.5711, $\alpha^{27}_D +0.07^\circ$ (1 dm., neat) and 0.79 g. of alcohol, n^{25}_D 1.5687, $[\alpha]^{25}_D +18.3^\circ$ (benzene, c 10.2), which were submitted to infrared and polarimetric analysis.

Formolysis of the Tosylates of the Isomeric 1,2-Diphenyl-2-methyl-1-butanols (II).—A solution of 1.0 liter, 25% C.P. alcohol-free chloroform-75% anhydrous formic acid (% by volume) and 3.7 g. of anhydrous sodium formate was titrated¹⁶ and found to be 0.0538 M in sodium formate. Kinetic measurements¹⁶ indicated the rates of formolysis of a mixture of the diastereomeric tosylates to be too fast to measure, the reaction being over in less than 2 minutes at

25° . The tosylate ester of (-)-*erythro*-II (6.9 g., run 4) was dissolved in 360 ml. of the above solution (immediate solution was observed), allowed to stand at 25° for two minutes, and was poured onto one l. of crushed ice-water mixture containing 10 ml. of saturated sodium chloride solution. The isolation procedure was the same as in the acetolysis, 4.05 g. of distilled olefin-alcohol being obtained (no residue from the olefin-formate distillation was observed). The olefin fraction amounted to 1.60 g., n^{25}_D 1.5714, $\alpha^{25}_D -0.26^\circ$ (1 dm., neat), and the alcohol, 1.42 g., n^{25}_D 1.5686, $[\alpha]^{25}_D -13.0^\circ$ (benzene, c 10.2).

Similar treatment (run 3) of 7.0 g. of (-)-*threo*-II gave 4.22 g. of olefin-alcohol mixture (distilled). No residue was obtained from the olefin-formate distillation. The olefin fraction amounted to 1.91 g., n^{25}_D 1.5710, $\alpha^{25}_D -1.71^\circ$ (1 dm., neat), and the alcohol fraction was 1.59 g., n^{25}_D 1.5683, $[\alpha]^{25}_D -17.7^\circ$ (benzene, c 10.1).

The olefin fractions from both solvolyses appeared to be unstable to air and could not be allowed to stand.

Ozonolysis of Olefins Obtained from Solvolyses.—The procedure is illustrated as applied to olefin from run 2. To olefin (1.0 g.) dissolved in 40 ml. of C.P. methylene chloride at 0° was added (bubbled through) ozone for one hour. After this time a rubber tube fitted to the exit tube showed signs of decomposition. The mixture was then added dropwise to a refluxing mixture of 1.0 g. of zinc dust, a crystal of silver nitrate and 50 ml. of distilled water. The resulting mixture was refluxed for 15 minutes, cooled and extracted with pentane. The pentane layer was washed, dried, evaporated, and the residue was distilled at 2 mm. (bath temperature 135°) to give 0.92 g. of a ketonic mixture, n^{25}_D 1.5703, $\alpha^{25}_D -0.11^\circ$ (1 dm., neat). A small amount of this material when treated with 2,4-dinitrophenylhydrazine reagent afforded after two recrystallizations of the product yellow needles, m.p. $137.8-139.2^\circ$, undepressed by admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of 1,1-diphenyl-2-propanone (m.p. 140° , see below for preparation).

The aqueous phase from the above ozonolysis decomposition reaction was filtered and was qualitatively tested for formaldehyde (Deniges method)^{17a} and acetaldehyde, (Ley reagent).^{17b} Both tests were positive, and appropriate controls established that the aldehydes did not come from solvent impurities.

Olefin (1.0 g.) from run 1 gave upon ozonolysis 1.0 g. of ketone, n^{25}_D 1.5760, $\alpha^{25}_D -0.22^\circ$ (1 dm., neat). Positive tests for acetaldehyde and formaldehyde were obtained.

Olefin (1.0 g.) from run 3 gave 0.88 g. of ketonic mixture, n^{25}_D 1.5722, $\alpha^{25}_D -1.60^\circ$ (1 dm., neat), whereas olefin (1.0 g.) from run 4 gave 0.95 g. of ketone, n^{25}_D 1.5730, $\alpha^{25}_D -0.39^\circ$ (1 dm., neat).

Reverse Condensation Reactions Run on Alcohol Fractions.—The procedure is illustrated as applied to a synthetic mixture of alcohols II and III. A mixture of potassium metal (0.111 g.) and 2 ml. of anhydrous N-methylaniline (distilled from potassium) was heated at 200° under nitrogen for two hours, cooled to 72° , and a solution of 0.214 g. of racemic 1,1-diphenyl-2-methyl-2-butanol (III, see below) and 0.451 g. of (+)-II (mixture of optically pure diastereomers, $[\alpha]^{25}_D +20.33^\circ$ (benzene, c 9.99) in 1 ml. of anhydrous N-methylaniline was added. The reaction mixture was stirred at 72° for 30 minutes, cooled to 0° , and the trace of unreacted potassium metal was decomposed with ethanolic N-methylaniline. The resulting mixture was shaken with 4 ml. of concentrated hydrochloric acid in 40 ml. of water, 20 g. of ice and pentane. The pentane extract was washed with acid, water, was dried and the solvent was evaporated. The resulting oil was chromatographed on 30 g. of Activity III neutral alumina¹⁵ made up in pentane. Development of the column with pentane gave eluent which upon distillation gave 0.106 g. (71%) of hydrocarbon which possessed an infrared spectrum identical to that of diphenylmethane. The alcohol was washed from the column with 100 ml. of C.P. methanol. The solvent was evaporated, the residue was taken up in pentane, and this solution was washed with water, dried and evaporated. Distillation of the residue (2 mm. and 145° bath temperature) gave 0.35 g. (77% recovery) of the same mixture of diastereomers of II that was used as starting material, $[\alpha]^{25}_D +20.1^\circ$ (benzene,

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c 9.32), n_D^{25} 1.5692. Utilizing a similar procedure, alcohol from run 1 (0.70 g.) gave 0.08 g. of hydrocarbon and 0.48 g. of II, $[\alpha]_D^{25} +19.3^\circ$ (benzene, *c* 10.1). Likewise alcohol from run 2 (0.76 g.) gave 0.11 g. of hydrocarbon and 0.55 g. of II, $[\alpha]_D^{25} +27.1^\circ$ (benzene, *c* 10.1). Alcohol from run 4 (1.42 g.) gave 0.59 g. of hydrocarbon and 0.21 g. of alcohol, n_D^{25} 1.5685, $[\alpha]_D^{25} -16.8^\circ$ (benzene, *c* 5.23). Alcohol from run 3 (1.59 g.) gave 0.74 g. of hydrocarbon and 0.28 g. of II, n_D^{25} 1.5685, $[\alpha]_D^{25} -32.9^\circ$ (benzene, *c* 9.2). In all four of these runs, the infrared spectra of the hydrocarbon fractions were virtually identical to that of diphenylmethane. The chromatographs in runs 3 and 4 were run slightly differently than in the same procedure. Hydrocarbon was eluted with pentane, a ketonic contaminant was eluted with 20% ether in pentane, and the alcohol was eluted with methanol. The ketonic fraction in each case formed a red 2,4-dinitrophenylhydrazone which after two recrystallizations from ethanol gave ca. 2 mg. of red crystals which melted over a range and lower than 100° .

Conversion of 1,2-Diphenyl-2-methyl-1-butanol (II) to 1,2-Diphenyl-2-methylbutane (IV).—The procedure is illustrated as applied to a mixture of optically pure diastereomers of II. Alcohol (1.0 g.), $[\alpha]_D^{25} +20.3^\circ$ (benzene, *c* 9.91) was dissolved in 10 ml. of C.P. anhydrous benzene, and treated with 0.168 g. of potassium metal and 0.79 g. of tosyl chloride as in the procedure recorded above for the preparation of the tosylates of II. The crude tosylate ester thus obtained was added to a slurry (stirred) of 1.32 g. of lithium aluminum hydride and 100 ml. of anhydrous ether. The resulting mixture was stirred for two hours and allowed to stand at room temperature for 12 hours. Wet ether now was added and then finally a cold solution of aqueous ammonium chloride. The organic layer was washed with water, dried and evaporated. The residue was chromatographed on 30 g. of Activity I neutral alumina¹⁵ made up in pure pentane. The desired product was eluted with 100 ml. of pure pentane, the solvent was evaporated, and the residual oil was distilled at 3 mm. and a bath temperature of 125° , wt. 0.55 g. This impure material was dissolved in 5 ml. of glacial acetic acid, 0.6 g. of 2,4-dinitrobenzenesulfonyl chloride was added and the resulting solution was heated at 100° for one hour. The reaction mixture was cooled and placed directly on a chromatographic column of 40 g. of activity III neutral alumina¹⁵ made up in pure pentane. The desired hydrocarbon was eluted with 100 ml. of pure pentane, the solvent was evaporated, and the residue was distilled to give 0.55 g. (59% yield) of (+)-1,2-diphenyl-2-methylbutane (IV), n_D^{25} 1.5550, $\alpha_D^{25} +66.3^\circ$ (1 dm., neat), d_4^{25} 0.9718, $[\alpha]_D^{25} +67.4^\circ$ (neat).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.95; H, 8.98.

Application of this procedure to 0.48 g. of the alcohol II obtained from run 1 gave 0.27 g. (60% yield) of optically pure hydrocarbon (IV), n_D^{25} 1.5542, $\alpha_D^{25} +66.40^\circ$ (1 dm., neat). From 0.55 g. of alcohol from run 2 was obtained 0.31 g. (60% yield) of optically pure IV, n_D^{25} 1.5547, $\alpha_D^{25} +66.5^\circ$ (1 dm., neat).

1,1-Diphenyl-2-propanone (XI).—This material was obtained in 55% yield¹⁸ (two recrystallizations from pentane), m.p. $59-60.2^\circ$ (reported¹⁸ m.p. $60-61^\circ$). The 2,4-dinitrophenylhydrazone was prepared as yellow needles (absolute ethanol), m.p. $138-139.6^\circ$ (reported¹⁸ m.p. 140°).

Anal. Calcd. for $C_{21}H_{18}N_4O_4$: C, 64.61; H, 4.65. Found: C, 64.66; H, 4.81.

1,1-Diphenyl-2-butanone (X).—Application of a reported procedure²⁰ to the preparation of 1,1-diphenyl-1-hydroxy-2-butanone gave material, m.p. $114-115.1^\circ$ (reported²⁰ m.p. 92°).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.33; H, 7.60.

Conversion of 5 g. of this glycol to X²⁰ gave 4.3 g. (97% yield) of product, n_D^{25} 1.5678. This material was converted to its semicarbazone, five recrystallizations of which (benzene) gave soft needles (50% yield), m.p. $187.6-189.8^\circ$,

reported m.p. $194-195^\circ$ ²¹ and 185° ²². Regeneration of the ketone X²³ (85% yield) gave X as a colorless liquid, n_D^{25} 1.5668. A 2,4-dinitrophenylhydrazone derivative was prepared, yellow needles (absolute ethanol), m.p. $118.2-119.8^\circ$.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.33; H, 4.98. Found: C, 65.22; H, 5.06.

(+)-1,2-Diphenyl-1-butanone.—Since this compound was a potential product of the rearrangement, it was prepared in optically pure form. Resolution of 2-phenylbutanoic acid²⁴ gave material, b.p. $130-132^\circ$ (4 mm.), n_D^{25} 1.5128, $[\alpha]_D^{25} +90.3^\circ$ (1 dm., neat), reported²⁴ $[\alpha]_D^{25} +89.9^\circ$ (1 dm., neat). The acid chloride was obtained from 9 g. of the acid and 16.5 ml. of thionyl chloride, and was allowed to react with diphenylcadmium prepared from 18.5 g. of bromobenzene, 2.83 g. of magnesium and 11.3 g. of anhydrous cadmium chloride in the usual manner.²⁵ The product was distilled through a 2.5-foot Podbielniak type of column to give 10.2 g. (83% yield) of ketone, b.p. $150-151^\circ$ (5 mm.), m.p. $54.2-57.8^\circ$. Recrystallization of this material (three times) from ethanol-pentane gave 4.3 g. of ketone, m.p. $57-58^\circ$, $[\alpha]_D^{25} +230.2^\circ$ (benzene, *c* 4.99).

Anal. Calcd. for $C_{18}H_{16}O$: C, 85.67; H, 7.14; Found: C, 85.48; H, 7.17.

Racemic 1,1-Diphenyl-2-methyl-2-butanone (III).—Ethyllithium was prepared from 5.29 g. of lithium metal, 41.6 g. of ethyl bromide and 300 ml. of anhydrous ether. The reagent was filtered through a cotton plug, cooled under nitrogen to 0° , and mixed with 16 g. of 1,1-diphenyl-2-propanone in 50 ml. of dry ether. The solution (yellow) was stirred at 0° for one hour, and ammonium chloride solution was added. The organic layer was washed with water, dried and evaporated. The residual oil was treated with 27.8 g. of Girard T reagent²⁶ dissolved in 278 ml. of 10% (by volume) glacial acetic acid-absolute ethanol solution for 45 minutes. The mixture was then shaken with water and pure pentane, the pentane was washed with water, dried and evaporated. The residue was chromatographed on 320 g. of neutral Activity III alumina¹⁵ made up in pure pentane. The column was washed with pentane, and developed with ether-pentane mixtures to give a number of fractions, each of which contained oil whose refractive indices and boiling points were virtually identical. This material was distilled (bath temperature $130-135^\circ$ at 1 mm.) to give 12.4 g. of alcohol, n_D^{25} 1.5687. The infrared spectrum of this material contained a carbonyl band of weak intensity at 1705 cm^{-1} .

When 5 g. of this material was treated with excess ethyllithium (6 mole ethyllithium to 1 mole "alcohol") at 25° for 4 hours there was obtained upon distillation of the crude reaction product 4.8 g. of the desired alcohol, n_D^{25} 1.5678. This material had no carbonyl absorption at 1705 cm^{-1} .

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.74; H, 8.33.

The acetate of this tertiary alcohol III was prepared as follows: Alcohol III (2.9 g.) was treated at $135-140^\circ$ for 68 hours with 12.3 g. of distilled acetic anhydride and 9.55 g. of pure pyridine. The black reaction mixture was shaken with pure pentane and dilute acid, the pentane layer was washed with acid solution, water, was dried and evaporated. The residue was chromatographed on 120 g. of Activity III neutral alumina¹⁵ made up in pure pentane. From the eluent obtained with 5% ether-pentane was obtained 2.08 g. of a colorless oil, n_D^{25} 1.5473 (after distillation at 2 mm., 135° bath temperature). Crystallization of this material from methanol at -80° gave white tablets, m.p. $42.3-43.8^\circ$.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.84; H, 7.86. Found: C, 80.89; H, 7.87.

Both olefin and starting alcohol were isolated from the other chromatographic fractions.

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(+)-*erythro*-1,2-Diphenyl-2-methyl-1-acetoxybutane.—From 2.25 g. of optically pure (+)-*erythro*-II, 9.48 g. of C.P. distilled acetic anhydride and 7.34 g. of pure pyridine (reaction at 135–140° for 10 hours) the product was obtained by the usual method. The crude acetate was dissolved in 10 ml. of pentane. After standing at –10°, the material crystallized as dense white tablets, m.p. 40–44°, 1.62 g. Recrystallization of the solid from pentane gave 1.5 g., m.p. 42.4–44°. Additional material (0.5 g.) was obtained by chromatography of the filtrates, m.p. 42.4–44°, total yield 75%, $[\alpha]_D^{25} + 8.93^\circ$ (benzene, *c* 4.71).

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.80; H, 7.86. Found: C, 80.98; H, 7.91.

(+)-*threo*-1,2-Diphenyl-2-methyl-1-acetoxybutane.—By a similar procedure except that a chromatographic purification was involved, 1.25 g. of (+)-*threo*-II gave 1.26 g. of its acetate as a colorless viscous oil, n_D^{25} 1.5476, $[\alpha]_D^{25} + 7.72^\circ$ (benzene, *c* 4.72).

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.80; H, 7.86. Found: C, 80.82; H, 7.75.

Other Materials for Infrared Analyses.—Benzophenone (commercial material) was recrystallized from ether–pentane to constant melting point, m.p. 52–54°. An analytical specimen of (–)-1,2-diphenyl-1-propanone was available from other studies,²⁷ m.p. 34–35°, $[\alpha]_D^{25} - 206^\circ$ (chloroform, *c* 4.2).

Control Experiments.—The olefin mixture (0.6 g., n_D^{25} 1.5706) obtained from run 2 was resubmitted to the whole acetolysis and isolation procedure to give 0.51 g. of recovered material (85%), n_D^{25} 1.5708. Ozonolysis of this olefin gave 0.51 g. of ketonic mixture, n_D^{25} 1.5752, α_D^{25} –0.05° (1 dm., neat). Similar ozonolysis of the original olefin gave ketone, n_D^{25} 1.5756, α_D^{25} –0.05° (1 dm., neat). The infrared spectra of the two ketone mixtures were identical.

An olefin mixture was obtained by chromatography of (–)-*threo*-II-tosylate on alumina, n_D^{25} 1.5750, α_D^{25} –0.06° (1 dm., neat). This material (0.35 g.) was also subjected to the acetolysis procedure and recovered, n_D^{25} 1.5750, α_D^{25} –0.06° (1 dm., neat). Both the original olefin and that subjected to the acetolysis procedure were converted to their ketones. The infrared spectra, indices of refraction and rotations of these two samples were essentially identical (n_D^{25} 1.5709 and α_D^{25} +0.40°, 1 dm., neat).

An olefin mixture obtained from the acetolysis of the tosylate of *rac*-*erythro*-II (0.50 g., n_D^{25} 1.5692) was submitted to the conditions of formolysis and recovered, wt. 0.45 g., n_D^{25} 1.5692.

A mixture of optically pure diastereomeric acetates of (+)-*threo*-II and (+)-*erythro*-II (1.0 g., n_D^{25} 1.5478, $[\alpha]_D^{25} + 8.31^\circ$ (benzene *c* 7.33) was subjected to the acetolysis conditions, and 0.90 g. of acetate was recovered, n_D^{25} 1.5482, $[\alpha]_D^{25} + 8.35^\circ$ (benzene, *c* 7.33). Reduction of this material with lithium aluminum hydride gave 0.70 g. of (+)-*threo* and (+)-*erythro*-II, n_D^{25} 1.5694, $[\alpha]_D^{25} + 35.4^\circ$ (benzene, *c* 10.06). This rotation corresponds to a composition of 58% (+)-*threo*-II and 42% (+)-*erythro*-II which corresponds to the composition of the original acetate mixture.

The tertiary acetate of III (0.50 g., n_D^{25} 1.5475) was submitted to the acetolysis procedure to give 0.42 g. of recovered acetate, n_D^{25} 1.5476, whose infrared spectrum was identical to that of the starting material. Submission of this acetate to the lithium aluminum hydride reduction procedure gave 0.30 g. of tertiary alcohol III, n_D^{25} 1.5680 (as compared to n_D^{25} 1.5678 of an authentic sample). The

infrared spectrum of this material was the same as that of III.

Attempts to prepare the formates of II and III failed, so analogous controls could not be applied to the formolyses.

Infrared Analyses of the Alcohol Fractions.—These analyses were performed with a Perkin–Elmer recording spectrophotometer, model 21. The samples were run in a 0.027-mm. cell (sodium chloride) as liquid films with a solid salt block of identical thickness to the cell windows as a blank. The instrument was balanced at 1355.5 cm^{-1} with response 1:1, gain 4.5, suppression 5, speed 0 and resolution 940. Table III records the optical densities of *threo*- and *erythro*-II and III at those wave lengths most advantageous for analysis, a synthetic mixture of the three components, and the alcohol fractions from the acetolyses. A similar type of data was obtained for the alcohol fractions from the formolysis which contain these three components, as well as for the alcohol fractions from the formolyses and acetolyses from which tertiary alcohol III had been removed.

Infrared Analysis of the Ketone Fractions from Olefin.—The same instrument and cells were employed, except the instrument was balanced at 1423.5 cm^{-1} . The total spectra of the ketonic mixtures from the acetolysis (runs 1 and 2) were nearly identical to one another, differing only slightly in the intensity of some peaks. The carbonyl region exhibited only two absorption maxima at 1705 and 1655 cm^{-1} , which correspond to unconjugated carbonyl and doubly conjugated carbonyl absorptions, respectively.²⁸ There was no absorption maximum that corresponded to singly conjugated carbonyl absorption²⁸ at 1680 cm^{-1} , and the sensitivity of the instrument to this type of compound was demonstrated with a synthetic mixture of ketones X, XI and XII to which only 8% of 1,2-diphenyl-1-propanone was added. This mixture exhibited significant optical density (0.75) at this wave length. Two absorption maxima at 1580 (conjugated phenyl absorption)²⁸ and 1355 cm^{-1} (acetyl group absorption)²⁸ further identified the components of the unknown mixtures as probably containing 1,1-diphenyl-2-propanone (XI) and benzophenone (XII). The amounts of X, XI and XII in these mixtures were estimated utilizing the “base line density” method²⁹ and synthetic mixtures and the optical densities at the following most advantageous wave numbers, X at 1105 cm^{-1} , XI at 1355 cm^{-1} and XII at 809 and 920 cm^{-1} .

TABLE III
DATA FOR INFRARED ANALYSIS OF ALCOHOL FRACTIONS OBTAINED FROM ACETOLYSIS (RUNS 1 AND 2)^a

Compound	Optical densities at cm^{-1}					
	885.0	895.0	1054.0	1145.0	1245.0	1355.5
(+)- <i>threo</i> -II	0.129	0.281	0.569	0.200	0.269	0.204
(+)- <i>erythro</i> -II	.214	.207	.880	.207	.252	.217
III	.066	.117	.278	.565	.223	.379
Alcohol run 1 ^a	.169	.212	.730	.281	.248	.244
Alcohol run 2 ^a	.150	.213	.650	.308	.248	.256
Synthetic mixt. ^b	.143	.216	.633	.323	.254	.261

^a Run numbers defined in Table I. ^b Footnote b, Table I.

The ketones from the formolyses (runs 3 and 4) were analyzed by the same methods, again no maximum at 1680 cm^{-1} being observed. The estimates of the three ketones in the four runs are recorded in Table II.

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