of dry benzene at 15°. The resulting mixture was stirred at 15° for one hour and at room temperature for two additional hours. The benzene was evaporated under reduced pressure at 20°, and the residual oil was shaken with 0.1 *N* sodium hydroxide for 30 minutes. The oil was then extracted into pure pentane, the pentane layer was dried and passed through a column of 150 g. of basic alumina. The column was washed with additional pentane until no more ester appeared in the eluates. The column eluate was evaporated to about 60 ml., and the pentane solution was cooled to −20° for ten hours. The heavy crystals that separated were collected and recrystallized from pentane to give 13.5 g. of the sulfonate ester. These esters decomposed upon melting, and the decomposition points were completely unreproducible, even on the same sample. Examples are given in Table I.

Reaction of Sodium Ethylate with the *p*-Bromobenzenesulfonates of Racemic *erythro*- and *threo*-2,5-Dimethyl-4-phenyl-3-hexanol (I).—To a solution of sodium ethylate (2.0 g. of sodium and 16 ml. of absolute ethanol) was added 3.4 g. of the *p*-bromobenzenesulfonate of racemic *threo*-I. The resulting solution was heated at 95° for 18 hours, cooled, and shaken with a mixture of cold water and pure pentane. The organic layer was washed with water, dried and treated with decolorizing carbon. The solvent was evaporated through a short column, and the residual oil was twice flash distilled at 18 mm. to give 1.50 g. of colorless oil, $n^{25}\text{D}$ 1.4946.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Calcd. for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 87.13; H, 10.44.

From the above analysis and the reagent it appears that the oil is about 60% olefin–40% ethyl ether (2,5-dimethyl-4-phenyl-3-ethoxyhexane).

A similar procedure was applied to the reaction of sodium ethylate with the *p*-bromobenzenesulfonate of *erythro*-I. From 4.25 g. of starting ester, 1.90 g. of product was obtained, $n^{25}\text{D}$ 1.4993.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Calcd. for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 87.14; H, 10.49.

This mixture would also appear to be about 60% olefin and 40% ethyl ether.

LOS ANGELES, CALIFORNIA

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

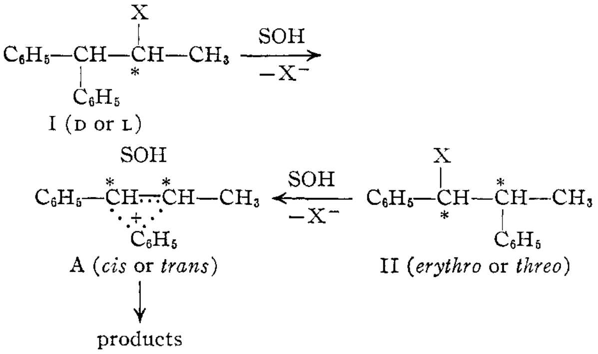
Studies in Stereochemistry. XXII. Rearrangement of the 1,1-Diphenyl-2-propyl into the 1,2-Diphenyl-1-propyl System[1]

BY DONALD J. CRAM AND FATHY AHMED ABD ELHAFEZ[2]

RECEIVED AUGUST 17, 1953

The preparation and resolution of 1,1-diphenyl-2-propanol and its derivatives are reported. Treatment of the optically pure (−)-alcohol with thionyl chloride produced a mixture from which optically pure D-*erythro*-1,2-diphenyl-1-propyl chloride was isolated. Attempts to prepare 1,1-diphenyl-2-propyl chloride from 1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate with lithium chloride in acetone gave 1,1-diphenyl-1-propene. Solvolysis of optically pure 1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate in acetic acid gave a mixture of partially racemic 1,1-diphenyl-2-propyl acetate, and of optically pure *threo*- and *erythro*-1,2-diphenyl-1-propyl acetates. The ratio of *threo* to *erythro* isomers was the same as that obtained from a solvolysis of *threo*-1,2-diphenyl-1-propyl *p*-bromobenzenesulfonate under the same conditions, a fact which suggests a common intermediate (a *trans*-phenonium ion) for the two processes. The mechanistic implications of these results are discussed.

This study constitutes a further inquiry into the mechanism of solvolytic reactions involving phenonium ion[3] intermediates,[4] particularly into the question of the relative ease of formation of diastereomerically related bridged ions. The 1,1-diphenyl-2-propyl (I) and 1,2-diphenyl-1-propyl (II) systems are capable of producing the same bridged ions A. Through the use of product analyses an attempt has been made to trace the stereochemical course of the various stages of these reactions.



Preparation and Reactions of the 1,1-Diphenyl-2-propyl System

The alcohol, 1,1-diphenyl-2-propanol (III), was resolved through the brucine salt of its acid phthalate to give the (−)-acid phthalate, whereas the (+)-isomer was freed from racemic material by fractional crystallization. That virtual optical purity was reached is indicated by the rotations and melting points of the enantiomeric alcohols, acid phthalates, *p*-nitrobenzoates, acetates and *p*-bromobenzenesulfonates that are reported in Table I. The preparation of the optically pure isomers of 1,2-diphenyl-1-propanol (IV) and its derivatives has been reported previously.[5]

In an attempt to form 1,1-diphenyl-2-propyl chloride, the *p*-bromobenzenesulfonate of III was treated with lithium chloride in acetone as solvent

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

(2) Postdoctoral Fellow of the University of Ibrahim, Cairo, Egypt, at the University of California at Los Angeles.

(3) Although the term "ethylenephenonium ion" would be more appropriate, since only this one kind of phenyl bridged ion has been considered so far in this series of papers, the abbreviated expression has been used.

(4) (a) D. J. Cram, THIS JOURNAL, **71**, 3863, 3875 (1949); (b) **74**, 2129, 2159 (1952); (c) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); (d) D. J. Cram, *ibid.*, **75**, 332 (1953); (e) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (f) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (g) S. Winstein, N. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (h) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165, 2171 (1953); (i) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953); (j) J. G. Burr, Jr., and L. S. Ciereszko, *ibid.*, **74**, 5426, 5431 (1952); (k) P. S. Bailey and J. G. Burr, Jr., *ibid.*, **75**, 2951 (1953).

(5) (a) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952); (b) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **74**, 5846 (1952); (c) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5851 (1952).

TABLE I

ANALYSES AND PHYSICAL PROPERTIES OF THE ISOMERS OF 1,1-DIPHENYL-2-PROPANOL (III) AND THEIR DERIVATIVES

Compound	Config.	M.p., °C.	Yield, %	$[\alpha]^{24-22}\text{D}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Alcohol	D	48–49 (58–59)[a]	93	+8.02°[b]	$C_{15}H_{16}O$	84.87	84.92	7.60	7.63
Alcohol	L	48–49 (58–59)[a]	94	−8.11[b]	$C_{15}H_{16}O$	84.87	84.75	7.50	7.70
Acid phthalate	D,L	185.5–186.5	94	....	$C_{23}H_{20}O_4$	76.65	76.90	5.59	5.47
Acid phthalate	D	143–144	30	+7.04[c]	$C_{23}H_{20}O_4$	76.65	76.77	5.59	5.52
Acid phthalate	L	143–144	34	−7.11[c]	$C_{23}H_{20}O_4$	76.65	76.40	5.59	5.58
p-Nitrobenzoate	D,L	119–120	96	....	$C_{22}H_{19}O_4N$	73.11	73.33	5.29	5.27
p-Nitrobenzoate	D	117.5–118[d]	94	−13.78[e]	$C_{22}H_{19}O_4N$	73.11	73.31	5.29	5.27
p-Nitrobenzoate	L	117.5–118[d]	95	+13.58[f]	$C_{22}H_{19}O_4N$	73.11	72.91	5.29	5.13
p-Bromobenzenesulfonate	D,L	99–100[g]	73	....	$C_{21}H_{19}O_3SBr$	58.47	58.45	4.44	4.67
p-Bromobenzenesulfonate	D	82–83	67	.......[h]	$C_{21}H_{19}O_3SBr$	58.47	58.60	4.44	4.55
p-Bromobenzenesulfonate	L	82–83	65	.......[h]	$C_{21}H_{19}O_3SBr$	58.47	58.76	4.44	4.31
Acetate	D,L	78–79	88	....	$C_{17}H_{18}O_2$	80.28	80.14	7.13	7.35
Acetate	D	Liq.	90	+45.7[i,j]	$C_{17}H_{18}O_2$	80.28	80.06	7.13	6.97
Acetate	L	Liq.	90	−45.4[i,k]	$C_{17}H_{18}O_2$	80.28	80.31	7.13	7.08

[a] The higher melting polymorph is obtained by allowing the lower melting form to solidify at 50°. [b] $CHCl_3$, *c* 9%. [c] $CHCl_3$, *c* 3%. [d] M.p. with racemic *p*-nitrobenzoate, 105–115°. [e] $CHCl_3$, *c* 11%. [f] $CHCl_3$, *c* 3%. [g] Melts with decomposition. M.p. depends on rate of heating. Reported for 4° per min. [h] Rotations not taken. [i] $CHCl_3$, *c* 5%. [j] $\alpha^{24}\text{D}$ 80.4° (l = 1 dm., neat). [k] $\alpha^{24}\text{D}$ −80.7° (l = 1 dm., neat).

and with lithium carbonate present as a second phase. The product was 1,1-diphenyl-1-propene (an authentic sample was prepared by dehydrating 1,1-diphenyl-1-propanol). Starting sulfonate ester was recovered in a control experiment in which the lithium chloride was omitted.

When mixed with thionyl chloride at 0°, 1,1-diphenyl-2-propanol (III) was converted to a mixture of *threo-* and *erythro*-1,2-diphenyl-1-propyl chlorides[5c] (V) in a ratio of 1.5 to 1. Repetition of the experiment with optically pure (−)-III gave a mixture of rearranged chlorides from which was isolated optically pure D-(−)-*erythro*-1,2-diphenyl-1-propyl chloride (V).[5c] Control experiments which show the persistence of these chlorides under the conditions of their formation were reported previously.[4e] The solubility characteristics of racemic and active *erythro*-1,2-diphenyl-1-propyl chloride are such that any racemic material would not have been lost with crystallization.[5c]

Optically pure samples of *p*-bromobenzenesulfonates of 1,1-diphenyl-2-propanol were solvolyzed in dry acetic acid in the presence of enough sodium acetate to neutralize the sulfonic acid produced. One run was made at 75° and two at 25°, the latter duplicating the conditions employed for the solvolyses of the *p*-bromobenzenesulfonates of 1,2-diphenyl-1-propanol reported previously.[4e] The acetate–olefin products were reduced with lithium aluminum hydride to alcohol–olefin mixtures, which were separated through chromatography. The alcohol fractions were analyzed as three component mixtures of 1,1-diphenyl-2-propanol (III) and *erythro-* and *threo*-1,2-diphenyl-1-propanol (IV), advantage being taken of the marked differences in the infrared spectra of the three alcohols.[6] Table II records the optical densities of the three pure alcohols (each racemate had a spectrum identical to its enantiomers) at the four wave lengths employed. The percentages of the three components in the unknown mixtures were first calculated (two sets of three simultaneous equations) assuming that Beer's law applied, and these values were corrected to known mixtures of the three components that approximated the composition of the unknown mixtures. The results are set forth in Table III. Control experiments with *threo-* and *erythro*-1,2-diphenyl-1-propyl acetate and 1,1-diphenyl-2-propyl acetate demonstrate that these esters persist under the conditions of their formation in run 1.

TABLE II

EXTINCTION COEFFICIENTS OF 1,1-DIPHENYL-2-PROPANOL (III) AND OF *threo-* AND *erythro*-1,2-DIPHENYL-1-PROPANOL (IV) IN THE INFRARED AT THOSE WAVE LENGTHS USED FOR ANALYSIS[a]

Compounds[b]	Slit width (mm.) →	Optical densities, μ[c] λ10.22 0.714	λ10.49 0.750	λ11.39 0.930	λ12.73 1.360
III		0.119	0.569	0.355	0.100
threo-IV		.518	.106	.083	.251
erythro-IV		.307	.083	.087	.475
Run 1[d] (AcOH, 75°)		.433	.115	.099	.312
{model, run 1 (64% *threo*-IV, 31% *erythro*-IV, 5% III)}		.423	.124	.104	.320
Run 2[d] (AcOH, 25°)		.308	.285	.203	.234
{model, run 2 (38% *threo*-IV, 20.5% *erythro*-IV, 41.5% III)}		.303	.304	.208	.240

[a] Beckman spectrophotometer, model IR2T, NaCl prism and cells. [b] Although the pure compounds are solids, they can be held at room temperature as supercooled liquids for short periods of time. [c] Liquid films, 0.03 mm. thick. [d] Run numbers same as Table III and text.

The relative configurations of the alcoholic products in runs 1 and 2 were demonstrated as follows. A sample of the alcohol mixture from run 1 was added to thionyl chloride at 0° to give a chloride mixture from which was isolated a 13% yield of D-(−)-*erythro*-1,2-diphenyl-1-propyl chloride[4e] that was 96.5% optically pure. This percentage is based on the rotation of chloride obtained by adding optically pure L-(−)-1,1-diphenyl-2-propanol[7] to thionyl chloride as discussed earlier. The material in the filtrate from the crystallization of the chloride was solvolyzed under equilibrating conditions[4e] to give a mixture of formates from which was isolated an over-all yield of 24% of D-(−)-*erythro*-1,2-diphenyl-1-propyl formate that was

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(6) These spectra have been reported previously (ref. 4e).

(7) This configurational assignment will be discussed later in the paper.

TABLE III

RESULTS OF ANALYSIS OF UNKNOWN MIXTURES FROM ACETOLYSES

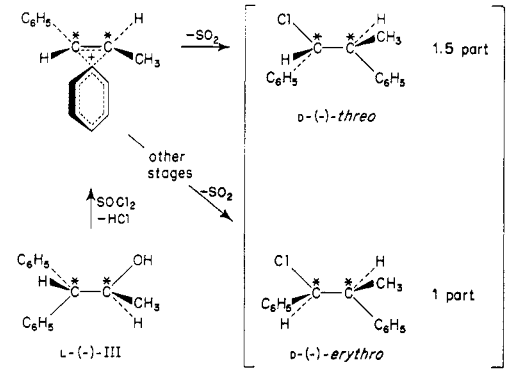
Run[a] no.	Starting material	Temp., °C.	Time, hr.	Yld. alc., %	$[\alpha]^{25}D$[b] alc.	Yld. olef., %	Composition of alcohols, %: λ = 10.22 III	10.49 IV threo	10.49 IV erythro	12.73 μ Total	λ = 10.22 III	11.39 IV threo	IV erythro	12.73 μ Total
1	L-(−)-III	75	19	80	−53.5°	15%	3.3	69	28	100	4.0	69	28	101
2	D-(+)-III	25	1076[c]	48	+32.6	..[c]	38	42	18	98	40	42	18	100
3[d]	L-(−)-III	25	504[c]	21	+32.1	..[c]	..	..	..	..	..	..	..	...

[a] Run numbers same as Table II and text. [b] c 5% $CHCl_3$. [c] All of the starting material was not used in this time. It was converted to hydrocarbon with $LiAlH_4$, which was isolated with olefin. [d] Not enough material obtained for infrared analysis.

97.4% optically pure.[8] Finally a synthetic mixture of 68.7% D-(−)-*threo*- and 27.7% D-(−)-*erythro*-1,2-diphenyl-1-propanols (IV) and 3.6% of racemic 1,1-diphenyl-2-propanol (III) was found to have $[\alpha]^{25}D$ −53.5° (c 5% in $CHCl_3$) as compared to $[\alpha]^{25}D$ −53.5° (c 6% in $CHCl_3$) for the mixture of propanols from the solvolysis in run 1. Furthermore, a synthetic mixture of 41.5% D-(−)-*threo*- and 18.5% D-(−)-*erythro*-IV and 40% of racemic III was found to have $[\alpha]^{25}D$ −32.4° (c 5% $CHCl_3$), whereas a mixture of the same composition except that the III employed was 10% enriched in the L-(−) isomer possessed $[\alpha]^{25}D$ −32.8° (c 5% $CHCl_3$). These rotations compare with $[\alpha]^{25}D$ +32.6 (c 5% $CHCl_3$) for the mixture of propanols from the solvolysis in run 2, and $[\alpha]^{25}D$ −32.1° (c 5% $CHCl_3$) for those from run 3. These experiments taken in conjunction with those reported previously[4e] that act as controls make it highly probable that in experiments 1 and 2, the rearranged 1,2-diphenyl-1-propyl acetates produced are virtually optically pure while the unrearranged 1,1-diphenyl-2-propyl acetate is somewhat racemic.

Discussion

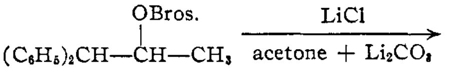
The results of the action of thionyl chloride on optically pure (−)-III to produce a mixture of D-(−)-*threo*- and D-(−)-*erythro*-1,2-diphenyl-1-propyl chlorides (only the latter was isolated when active III was employed) allows the configurations of (+)- and (−)-III to be assigned relative to D-glyceraldehyde. This assignment follows from: (1)



the configurations of the chloride products which have been demonstrated previously[5a,5b]; (2) the stereochemical course of the thionyl chloride reaction which has been thoroughly studied in similar systems[4d,4e]; (3) the use of D-lactic acid as a conventional model for III.

D-(−)-lactic acid D-(+)-III

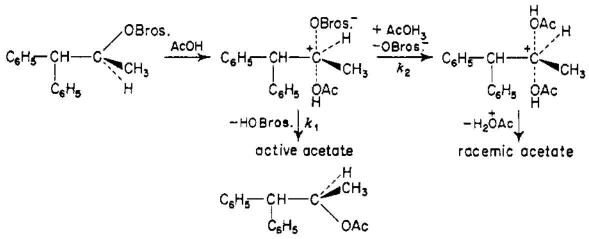
The failure of 1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate to enter into a substitution reaction with lithium chloride is similar to the behavior of aryl sulfonate esters of the isomers of 3-phenyl-2-butanol (unpublished results). The interesting



$$(C_6H_5)_2CH-\overset{\text{OBros.}}{CH}-CH_3 \xrightarrow[\text{acetone} + Li_2CO_3]{LiCl} (C_6H_5)_2C{=}CH-CH_3$$

features of this elimination reaction are the necessity of the presence of lithium chloride and the fact that unrearranged olefin was produced. The stereochemistry of this reaction is being studied in other systems.

Any mechanism proposed for the acetolyses of the *p*-bromobenzenesulfonate of the isomers of III (runs 1–2) must accommodate the facts summarized in Chart I. Thus the somewhat racemic character of the unrearranged product (III) points to the disolvated open ion as an intermediate, and indicates that k_1 is not > k_2. The optical purity of the re-



arranged product (1,2-diphenyl-1-propanol) in these same runs is evidence for the concerted formation of a phenonium ion as a process competing with that of the formation of a solvated open ion pair, and evidence against the formation of the bridged ion from a symmetrical species (*e.g.*, the unrearranged disolvated open ion).

The most striking results are found in runs 2 and 8 (AcOH, 25°) in which the same ratio of *threo*- to *erythro*-1,2-diphenyl-1-propanol was obtained from two different starting materials. This observation points strongly to the formation of a common intermediate from the *p*-bromobenzenesulfonates of L-1,1-diphenyl-2-propanol and D-*threo*-1,2-diphenyl-1-propanol. It further suggests that essentially all of the 1,2-diphenyl-1-propanol formed in the two reaction schemes arises from a common precursor or precursors. Since these products in each case are optically pure, this intermediate must secure asymmetry at the carbon atom which in the

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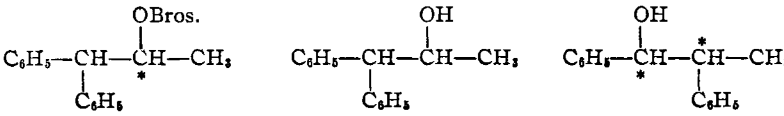
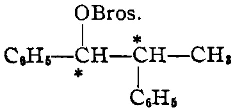
[8] It was demonstrated earlier (ref. 4e) that either optically pure *erythro*- or *threo*-1,2-diphenyl-1-propyl chloride goes to an equilibrium mixture of optically pure *erythro*- and *threo*-formates when solvolyzed.

CHART I



$C_6H_5{-}\underset{C_6H_5}{CH}{-}\overset{OBros.}{\underset{*}{CH}}{-}CH_3$ $C_6H_5{-}\underset{C_6H_5}{CH}{-}\overset{OH}{CH}{-}CH_3$ $C_6H_5{-}\overset{OH}{\underset{*}{CH}}{-}\underset{C_6H_5}{\overset{*}{CH}}{-}CH_3$

Config.		%	Opt. char.	%	Opt. char.	*threo/ erythro*
Bros. of L-(−)-III (run 1)	$\xrightarrow[\text{2, LiAlH}_4]{\text{1, AcOH NaOAc, 75°}}$	3–4	∼racemic	96	Opt. pure	2.47
Bros. of D-(+)-III (run 2)	$\xrightarrow[\text{2, LiAlH}_4]{\text{1, AcOH NaOAc, 25°}}$	40	∼racemic	60	Opt. pure	2.33



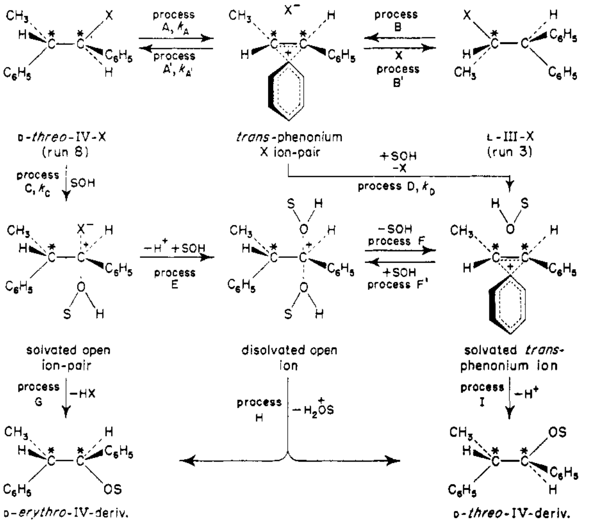
$C_6H_5{-}\overset{OBros.}{\underset{*}{CH}}{-}\underset{C_6H_5}{\overset{*}{CH}}{-}CH_3$

Config.						
D-*threo* (run 8)[4e]	$\xrightarrow[\text{2, LiAlH}_4]{\text{1, AcOH NaOAc, 25°}}$	0	...	..	Opt. pure	2.33
L-*erythro* (run 7)[4e]	$\xrightarrow[\text{2, LiAlH}_4]{\text{1, AcOH NaOHc, 25°}}$	0	...	..	Opt. pure	1.7

product carries the phenyl, methyl and hydrogen. Since the ratio of *threo* to *erythro* product differs when *threo-* and *erythro*-1,2-diphenyl-1-propyl *p*-bromobenzenesulfonate are the starting materials, then this intermediate must also be capable of maintaining partial asymmetry at the carbon that in the product carries the phenyl, hydrogen and hydroxyl groups. Furthermore, this intermediate must be incapable of producing 1,1-diphenyl-2-propanol as product, otherwise this product would have been obtained in run 8.

These observations are interpreted in the mechanistic scheme of Chart II. Here the precursor common to essentially all of the 1,2-diphenyl-1-propyl products of runs 2 and 8 (Chart I) is either the *trans*-phenonium-X ion-pair[9] alone, D-*threo*-IV-X alone, or both of these species. These three possibilities are consistent with the results only under the following sets of conditions. (1) The *trans*-phenonium ion-pair and not the D-*threo*-IV-X could be the common precursor only if $k_A >> k_C$ and $k_D >> k_A'$, an improbable situation in view of the fact that in other systems the rates of collapse to exchange of phenonium X ion-pairs in acetic acid is from 5 to 7.[4f] (2) If D-*threo*-IV-X alone is the precursor common to the products in question, then $k_D > > k_A'$, an equally unlikely situation for the same reason (see above). (3) The probability is that both D-*threo*-IV-X and the *trans*-phenonium-X ion-pair are the common precursors in question, and that $k_A > k_C$. A similar relationship between rate constants was found in both the *threo*-3-phenyl-2-butyl and 4-phenyl-3-hexyl systems, in spite of the fact that here *cis*-phenonium ions were involved.[4f] Thus the preferred mechanism involves the rapid establishment of a reversible reaction between D-*threo*-IV-X and *trans*-phenonium-X ion-pair, followed by the relatively slow dissipation of these two species by a number of different processes.[10]

CHART II



Although the disolvated 1,1-diphenyl-2-propylcarbonium ion does not go to the phenyl bridged ion, this does not rule out the possibility of the disolvated 1,2-diphenyl-1-propylcarbonium ion doing so (process F), since the internal distribution of charge of the latter ion makes external distribution of charge less important. Furthermore, the partial bonds between the ion and solvent would be weaker, the ion would have a longer half-life, and the phenyl on the adjacent carbon would have a better chance of displacing solvent. Thus five over-all processes exist in the scheme of Chart II for the production of product, processes A–D–I and C–E–F–I leading to *threo* material, process C–G going to *erythro* material, and process C–E–H and A–D–E'–H giving a mixture of *threo* and *erythro* product.

The high preference for migration that one phenyl shows over the other in run 2 provides the first case of this type of stereospecificity that has been found in the Wagner–Meerwein rearrangement, although a number of such cases are found in the work of McKenzie and Curtin on the pinacol and pinacol-like reactions.[11] An explanation similar to that of Curtin[11] that the sum of the steric repulsions (CH_3 >—< H and C_6H_5 >—< H) in a *trans*-phenonium ion are less than that of a *cis*-phenonium ion (CH_3

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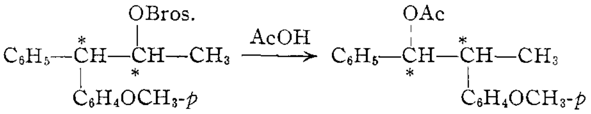
[9] In Chart II the phenonium ion is written with the phenyl half way between the two asymmetric carbon atoms. Other possibilities exist (ref. 4f), but are omitted for simplicity's sake.

[10] The intramolecular isomerization reaction represented by process B-A' is similar to that observed in the 3-phenyl-2-butyl, 3-phenyl-2-pentyl and 2-phenyl-3-pentyl systems (ref. 4b), in the 4-phenyl-3-hexyl system (ref. 4f), and the 2-phenyl-1-propyl system (ref. 4h).

[11] P. I. Pollak and D. Y. Curtin, THIS JOURNAL, **72**, 961 (1950); D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 992 (1951); D. Y. Curtin, E. E. Harris and P. I. Pollak, *ibid.*, **73**, 3453 (1951); D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952).

>—< C_6H_5 and H >—< H) would appear to apply. The interesting case where this steric advantage was overcome by the greater migratory ability of a *p*-methoxyphenyl over a phenyl has recently been reported.[12] Thus the reaction



$$C_6H_5-\overset{*}{C}H(C_6H_4OCH_3\text{-}p)-\underset{*}{C}H(\text{OBros.})-CH_3 \xrightarrow{\text{AcOH}} C_6H_5-\underset{*}{C}H(\text{OAc})-\overset{*}{C}H(C_6H_4OCH_3\text{-}p)-CH_3$$

VI (*erythro* or *threo*) VII

VI → VII was studied, the isomer that gives a *trans*-phenonium ion solvolyzing 1.8 times as fast as that giving a *cis*-phenonium ion.

Experimental

The Resolution of 1,1-Diphenyl-2-propanol (III).—The phthalic acid ester was prepared from the alcohol[4e] in the usual way (procedure B)[13] in 94% yield (see Table I). A mixture of 73 g. of this half-ester and 75 g. of brucine was dissolved in about 300 ml. of boiling acetone. To this hot solution water was added dropwise until the solution became slightly turbid. After standing at room temperature for several hours, the mixture deposited salt as needles, which were recrystallized from acetone and water five times. The filtrates were carried through four complete cycles of fractional recrystallization of the salt to furnish more material. The combined samples of salt were shaken with ether and ice-cold dilute sulfuric acid, the ether layer was washed with water, dried and evaporated. The residual oil was crystallized from ether–pentane to give 25 g. of pure acid phthalate, m.p. 142–143°, $[\alpha]^{26}\mathrm{D}$ −7.0° ($CHCl_3$, *c* 3.6%). The material was hydrolyzed (procedure A)[12] to give 13.2 g. of L-(−)-III, m.p. 48.5–49.5° (from pentane at 0°), $[\alpha]^{26}\mathrm{D}$ −8.11° ($CHCl_3$, *c* 9%). A small sample of the original brucine salt was submitted to nine instead of five recrystallizations and converted to the acid phthalate, m.p. 142–143°, $[\alpha]^{25}\mathrm{D}$ −6.2° ($CHCl_3$, *c* 10%).[14] This material was hydrolyzed to the free alcohol, m.p. 48.5–49.5°, $[\alpha]^{27}\mathrm{D}$ −8.2° ($CHCl_3$, *c* 9%).

The filtrates (rich in the other enantiomer) from the brucine salt recrystallizations were converted by the usual method to the phthalic acid ester, which was crystallized (70 ml. of ether) at room temperature to give a crop of essentially racemic material, wt. 5.0 g., m.p. 184.5–186.5°. The filtrate was treated with pentane to give the (+)-isomer which after four recrystallizations from ether–pentane afforded pure material, m.p. 142.5–143.5°, wt. 22 g., $[\alpha]^{25}\mathrm{D}$ +6.8° ($CHCl_3$, *c* 4%). This half-ester was hydrolyzed (procedure A)[13] to give 12.3 g. of D-(+)-III, m.p. 58–59°, $[\alpha]^{25}\mathrm{D}$ +8.05 ($CHCl_3$, *c* 9%).

The three samples of III (racemic, D and L) were converted to their respective *p*-nitrobenzoates (procedure B,[13] crystallized from ether–pentane), *p*-bromobenzenesulfonates (procedure C,[13] crystallized from pentane) and acetates (see below). The physical properties and analyses of these compounds are found in Table I. The acetates were prepared by the pyridine–acetic anhydride method, extracted into pure pentane, the solutions being thoroughly washed with dilute acid, dilute base and finally water. The pentane solutions were passed through a short column of alumina, and the column filtrates were evaporated to oils. The racemic acetate was crystallized from pentane. The active acetates were flash distilled twice at 25 mm. to give $n^{25}\mathrm{D}$ 1.5462 for the (−)-isomer and $n^{25}\mathrm{D}$ 1.5460 for the (+)-isomer.

Treatment of 1,1-Diphenyl-2-propanol (III) with Thionyl Chloride.—To 100 g. of pure thionyl chloride at 0° was added dropwise 21.2 g. of racemic III. After standing for 24 hours at room temperature, the mixture was stirred with crushed ice and extracted with ether. From here on the procedure is identical with that reported previously (procedure A).[4e] In the present experiment, 7.5 g. (33% yield) of racemic *erythro*-1,2-diphenyl-1-propyl chloride (m.p. 139–140°, m.m.p. with authentic materials[4e] 139–140°) was isolated as well as 11 g. (50% yield) of racemic *threo*-1,2-diphenyl-1-propyl chloride, m.p. 50–52°, m.m.p. with authentic material,[4e] 51–52°.

The experiment was repeated with 4.24 g. of (−)-III and 27 g. of thionyl chloride as starting materials. A 34% yield (1.6 g.) of D-*erythro*-1,2-diphenyl-1-propyl chloride was isolated, $[\alpha]^{25}\mathrm{D}$ −98.2° ($CHCl_3$, *c* 4%), m.p. 140–141°, m.m.p. with authentic material,[4e] 140–141°. No attempt was made to isolate the *threo* isomer.

Reaction of Lithium Chloride with the *p*-Bromobenzenesulfonate of 1,1-Diphenyl-2-propanol (III).—A mixture of 6.5 g. of the racemic sulfonate ester, 7.0 g. of anhydrous lithium carbonate, 10.0 g. of anhydrous lithium chloride and 300 ml. of dry acetone was held at reflux for 20 hours (the lithium chloride went into solution and the lithium carbonate remained as a second phase). The solvent was then evaporated, and the residue was shaken with a mixture of pure pentane and ice-water. The organic layer was washed with water, dried and the solvent was evaporated to a small volume without heat. The residual oil was cooled to 0°, and the solid that separated was collected, m.p. 45–47°, m.m.p. with authentic 1,1-diphenyl-1-propene (see below) 46–48°.

The above experiment was repeated with 6.5 g. of the sulfonate ester, 7.0 g. of lithium carbonate and 300 ml. of dry acetone (the lithium chloride was omitted). Starting material (6.0 g.) was isolated, m.p. 99–100°, m.m.p. with authentic material 97–99°.

An authentic sample of 1,1-diphenyl-1-propene[15] was prepared as follows. A mixture of 19 g. of 1,1-diphenyl-1-propanol[16] (m.p. 90–91°), 42 g. of acetic anhydride and 20 g. of practical acetyl chloride was heated at reflux for 22 hours. The product was mixed with crushed ice. The resulting mixture was extracted with ether, the ether solution was washed with dilute base and water, and dried. The solvent was evaporated and the residue was flash distilled at reduced pressure. The distillate was crystallized from pentane to give 8.1 g. of pure 1,1-diphenyl-1-propene, m.p. 48–48.6°. Mixed melting points with *cis*- and *trans*-1,2-diphenyl-1-propene[5c] gave substantial depressions (2,3-diphenyl-1-propene and 3,3-diphenyl-1-propene are both liquids at room temperature, unpublished work).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.82; H, 7.25.

Acetolysis of the *p*-Bromobenzenesulfonates of D- and L-1,1-Diphenyl-2-propanols (III). Run 1.—To a 0.25 *N* solution of potassium acetate in dry acetic acid containing 2% of acetic anhydride (100 ml.) which was held at 75° was added 8.63 g. (0.020 mole) of L-1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate. The resulting solution was held at 75° for 19 hours, cooled and shaken with a mixture of pure pentane (200 ml.) and water (500 ml.). The organic layer was washed twice with water, once with dilute base and dried. The pentane was evaporated through a short column, and the residual oil was added dropwise to a mixture of 1.0 g. of lithium aluminum hydride in ether. The excess hydride was decomposed with ethyl acetate, and the resulting mixture was shaken with ice-cold dilute hydrochloric acid and washed with dilute base and water, and was dried. The solvent was evaporated through a short column, and the residual oil was flash distilled. The distillate was submitted to chromatographic absorption on a 2.5 × 24 cm. column of activated alumina made up in pure pentane. The olefin was eluted with pure pentane (the progress of the band was followed with an infrared lamp), the pentane was evaporated through a short column, and the olefinic product was flash distilled, wt. 0.61 g. The alcohol fraction was eluted from the column with pure methanol, the methanol was evaporated through a small column to a small volume, and this solution was shaken with pure pentane and water. The pentane layer was washed with water, dried, and the solvent was evaporated through a short column. The residue was twice flash distilled, wt. 3.40 g., $[\alpha]^{27}\mathrm{D}$ −53.5° ($CHCl_3$, *c* 6%). This material was used directly in the infrared analysis scheme. The synthetic mixture that served as a model (for rotation) for the above was prepared from D-(−)-*threo*-1,2-diphenyl-1-propanol, $[\alpha]\mathrm{D}$ −46.8°

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[12] D. Y. Curtin and A. Bradley, Thirteenth National Organic Chemistry Symposium of the American Chemical Society, June, 1953, Ann Arbor, Mich.

[13] D. J. Cram, F. A. Abd Elhafez and H. Weingarten, THIS JOURNAL, **75**, 2293 (1953).

[14] This rotation changes slightly with concentration.

[15] A. Klages and S. Heilmann, *Ber.*, **37**, 1450 (1904).

[16] C. Hall and H. Bauer, *ibid.*, **37**, 231 (1904).

($CHCl_3$, *c* 5%) and D-(−)-*erythro*-1,2-diphenyl-1-propanol, $[\alpha]_D$ −70.0° ($CHCl_3$, *c* 5%).

The alcoholic mixture (1.0 g.) from the solvolysis of run 1 was added dropwise to 10 ml. of thionyl chloride at 10°. The solution was held at room temperature for six hours and worked up by the procedure reported previously (procedure A)[4e] to give 0.128 g. of D-*erythro*-1,2-diphenyl-1-propyl chloride, m.p. 138–139.5°, $[\alpha]^{25}_D$ −94.7° ($CHCl_3$, *c* 5%). The combined filtrates from the crystallization of this material was shaken with a mixture of water and pure pentane. The pentane layer was washed three times with water, dried and the pentane was evaporated to an oil. This oil was submitted to formolysis in dry solvent under the conditions of the formolyses of the 1,2-diphenyl-1-propyl chlorides (25°).[4e] The reaction mixture was worked up as follows. The solution was shaken with a mixture of pure pentane and water, the organic layer was washed twice with water and once with dilute base. The solution was dried, the solvent was evaporated until 5 ml. of solution remained, and the mixture was cooled to −10°. The formate that crystallized (D-*erythro*-1,2-diphenyl-1-propyl formate)[4e] was recrystallized from pentane to give 0.27 g. of ester, m.p. 87.5–87.8°, $[\alpha]^{25}_D$ −85.9° ($CHCl_3$, *c* 10%).

The acetolyses reported in runs 2 and 3 were carried out under conditions identical to those employed for the solvolyses of the *p*-bromobenzenesulfonate esters of *erythro*- and *threo*-1,2-diphenyl-1-propanol reported previously,[4e] except that the times were longer (see Table III), and not all of the starting material was consumed. What starting material remained, however, was converted to hydrocarbon during the lithium aluminum hydride treatment. The residues from the flash distillations of the alcohols were non-acidic. In run 2, from 4.9 g. of starting ester, 1.15 g. of alcoholic mixture was obtained, $[\alpha]^{25}_D$ +32.6° ($CCHl_3$, *c* 5%). The synthetic mixture that served as model (for rotations) was prepared from the same samples of alcohol that were used for the model for run 1.

Control Experiments for Acetolysis.—A solution of 1.35 g. of L-1,1-diphenyl-2-propyl acetate, n^{25}_D 1.5462, α^{24}_D −80.7° (neat, *l* = 1 dm.), in 26.5 ml. of dry acetic acid (containing 2% of acetic anhydride and 0.05 *N* in potassium acetate) was held at 75° for 19 hours. The mixture was then cooled and shaken with a mixture of pure pentane and water. The organic layer was washed with water (three times), and with dilute base. The solution was dried, the solvent was evaporated, and the residual oil was twice flash distilled at 25 mm. to give 1.27 g. of starting material, n^{25}_D 1.5462, α^{24}_D −79.9° (neat, *l* = 1 dm.).

The compound D-*threo*-1,2-diphenyl-1-propyl acetate[4e] (1.35 g.), $[\alpha]^{25}_D$ −7.1° ($CHCl_3$, *c* 8.5%), n^{25}_D 1.5412, was submitted to the above procedure to give 1.23 g. of starting material, $[\alpha]^{25}_D$ −7.0° ($CHCl_3$, *c* 8%), n^{25}_D 1.5411.

Acknowledgment.—A number of rotations and isolation experiments were carried out with the assistance of Mrs. Theodora W. Greene.

LOS ANGELES, CALIFORNIA

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

Reductive Polymerization of α,β-Unsaturated Amides. I. N,N-Diethylcrotonamide

BY H. R. SNYDER AND ROBERT E. PUTNAM[1]

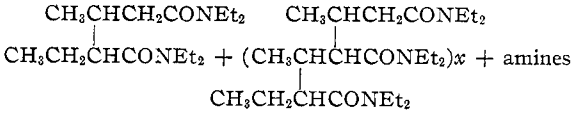
RECEIVED JULY 6, 1953

The treatment of N,N-diethylcrotonamide with lithium aluminum hydride, in molar equivalent of one-half or less, brings about reductive dimerization and polymerization of the amide. The structure of the dimeric reduction product is proved to to be that of N,N,N′,N′-tetraethyl-α-ethyl-β-methylglutaramide. The carbon chains of the polyamides produced probably are of the same type as the chain in the glutaramide. Especially when a relatively high molar proportion of the reducing agent is employed some reduction of amide groups occurs leading to mixtures of amines.

The reduction of amides by lithium aluminum hydride has proved useful for the preparation of amines.[2,3] In general the reduction of amides is carried out with an excess of the hydride and over a long reaction time. Under such conditions amides of unsaturated acids are reduced to saturated amines.[4]

It now has been found that upon treatment with small amounts of lithium aluminum hydride, N,N-diethylcrotonamide undergoes reductive *coupling* yielding N,N,N′,N′-tetraethyl-α-ethyl-β-methylglutaramide (I) along with a low molecular weight polymeric amide, probably of the structure shown by II. Reduction of amide groups also occurs, especially at relatively high ratios of the hydride to the amide, leading to a complex mixture of amines. The course of the reaction can be controlled within certain limits as shown in Table I.

$$CH_3CH{=}CHCONEt_2 \xrightarrow[\text{Ether}]{LiAlH_4}$$



$$\begin{array}{c} CH_3CHCH_2CONEt_2 \\ | \\ CH_3CH_2CHCONEt_2 \end{array} + \left(\begin{array}{c} CH_3CHCH_2CONEt_2 \\ | \\ CH_3CHCHCONEt_2 \\ | \\ CH_3CH_2CHCONEt_2 \end{array}\right)_x + \text{amines}$$

I II, $x > 0$

When one-half of a molar equivalent of lithium aluminum hydride is used all three products (dimer, polymer and amines) are produced, but with one-twentieth of an equivalent of the hydride, only the polymeric amide can be isolated.

The structure of the dimeric coupling product was proved by hydrolysis to the disubstituted glutaric acid III. After two recrystallizations the acid melted at 97–99°, and subsequent recrystallizations did not affect this value. Since the melting point is near that (101°) reported by Michael and Ross[5] for one of the diastereoisomeric α-ethyl-β-methylglutaric acids, the preparation described by these authors was repeated, with certain modifications. The synthesis consists in the addition of ethyl cyanoacetate to ethyl crotonate to yield diethyl α-cyano-β-methylglutarate (IV). Ethylation of IV with ethyl iodide yielded diethyl α-cyano-α-ethyl-β-methylglutarate (V), which on hydrolysis and decarboxylation with 20% hydrochloric acid gave a mixture of the diastereoisomeric α-ethyl-β-methyl-

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[1] National Science Foundation Fellow, 1952–1953.

[2] W. E. Brown, R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469; U. Solms, *Chimia*, **5**, 25 (1951).

[3] For an extensive study of the reduction of amides with this reagent, which appeared while this paper was in press, see V. Mićović and M. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

[4] A. Uffer and E. Schlittler, *Helv. Chim. Acta*, **31**, 1397 (1948).

[5] A. Michael and J. Ross, THIS JOURNAL, **53**, 1150 (1931).