covered; wt. 0.270 g., n^{25}_{D} 1.4878, α^{25}_{D} −12.3° (*l* 1 dm., neat).

As a control for those runs in which potassium *t*-butoxide was the base and 1-methoxy-1-phenylethane (XVI) was the product, the following experiment was carried out. A 0.23 molar solution of potassium *t*-butoxide in dioxane was prepared, and 25 ml. of this solution was mixed with 0.35 g. of XVI, n^{25}_{D} 1.4882, α^{24}_{D} +35.6° (*l* 1 dm., neat). The resulting solution was heated in a heavy-walled sealed tube to 190° for 26 hours. Recovery of XVI in the usual way gave 0.245 g. of material, n^{25}_{D} 1.4884, α^{23}_{D} +34.4° (*l* 1 dm., neat). Racemization occurred to the extent of 3%. The solution was twice as concentrated as any runs of this type recorded in Table V, and this control was carried out 40° higher in temperature.

As a control for those runs carried out with potassium diethylene glycoxide as base, the following experiment was carried out. A 0.11 *M* solution of potassium diethylene glycoxide in diethylene glycol was prepared, and 25 ml. was mixed with 0.25 g. of XVI, n^{25}_{D} 1.4882, α^{24}_{D} +35.6° (*l* 1 dm., neat). The solution was held at reflux at 245° for 16 hours, and XVI recovered in the usual way, n^{25}_{D} 1.4888, α^{23}_{D} +36.1° (*l* 1 dm., neat). No material racemized during this treatment.

Control runs reported previously[2b] apply to other experiments of this paper.

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO, AND DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

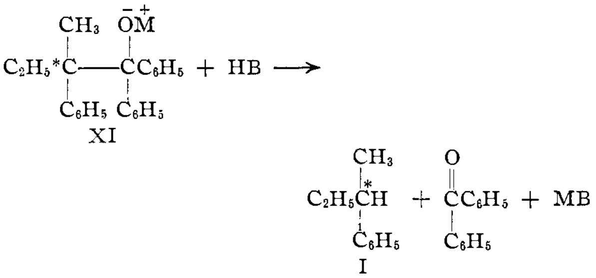
Electrophilic Substitution at Saturated Carbon. IV. Competing Radical and Anionic Cleavage Reactions[1]

BY DONALD J. CRAM,[2] ALBERT LANGEMANN, WALTER LWOWSKI AND KARL R. KOPECKY

RECEIVED JANUARY 2, 1959

The base-catalyzed cleavage of optically pure (+)-2-methyl-1,1,2-triphenyl-1-butanol has been studied in a variety of solvents. The compound has been shown to undergo reversibly a homolytic cleavage reaction to give 2-phenyl-2-butyl radical and the ketyl of benzophenone (radical anion) which both dimerize. This homolytic reaction competes with a heterolytic anionic cleavage which results in 2-phenylbutane and benzophenone. The effects of solvent and metal cation on these cleavages have been examined. The radical cleavage leads only to racemic products, whereas the anionic cleavage gives from 99% retention to 36% inversion in the accompanying electrophilic substitution at saturated carbon. The base-catalyzed cleavage of racemic 1,1,2-triphenyl-2-methoxy-1-propanol was found to give products which also indicated competing homolytic and heterolytic cleavage reactions. Cleavage of (+)-2-cyclohexyl-1,2-diphenyl-2-methyl-1-butanol gave only racemic 2-cyclohexylbutane in basic ethylene glycol and in basic *t*-butyl alcohol. Evidence is presented which suggests the reaction proceeds by a radical process.

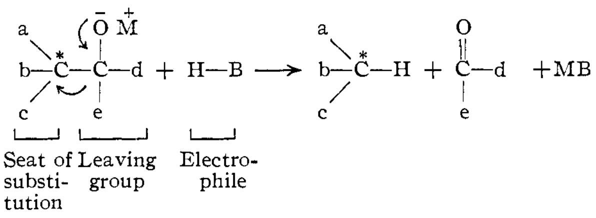
This paper is concerned with the mechanism and steric course of the base-catalyzed cleavages of (+)-2-methyl-1,1,2-triphenyl-1-butanol [(+)-XI], and of structural relatives of XI in which the substituents on the asymmetric carbon of the substances are varied. Cleavage reactions of compounds related to XI have been studied in previous papers of this series,[3] with major emphasis being placed on the factors which controlled the stereochemical course of the over-all electrophilic substitution which occurs at the benzyl carbon atom. In the past studies it seemed clear from the nature of reactants, products and conditions that the cleavage stage of these reactions involved a heterolytic and anionic process which can be generally described as in the formulation



$$\mathrm{C_2H_5\overset{*}{C}(CH_3)(C_6H_5)\text{—}C(\overset{-}{O}\overset{+}{M})(C_6H_5)C_6H_5 + HB \longrightarrow C_2H_5\overset{*}{C}H(CH_3)(C_6H_5) + (C_6H_5)_2C{=}O + MB}$$

XI

I



Compound XI seemed to be a particularly good system to study for a number of reasons. (1) The cleavage reaction occurs at somewhat lower temperatures than systems in which d and e of the leaving group are other than phenyl. (2) Benzophenone is formed in this reaction in good yield, and is not subject to base-catalyzed condensation reactions which might liberate water to the medium. (3) The appearance of benzophenone might be followed spectroscopically, and kinetic measurements made. (4) Unlike systems in which d or e are methylene groups, systems with d and e as phenyl groups have no internal proton source available to the carbanion created in the reaction.

Cleavage Reactions of (+)-2-Methyl-1,1,2-triphenyl-1-butanol [(+)-XI].—Optically pure starting material (XI) was reported previously[3a] and its configuration relative to that of I established.[3a,3c] The results of cleavage reactions of this system are recorded in Table IX. In run 82 a 66% yield of 2-phenylbutane (I) was obtained, the reaction having occurred with 60% predominating retention of configuration. This run differed in a number of important respects from those carried out in the

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

(2) Visiting Professor at the Instituto de Quimica, Universidad Nacional Autónoma de México, summer of 1956.

(3) (a) D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, THIS JOURNAL, **81**, 5740 (1959); (b) D. J. Cram, A. Langemann and F. Hauck, *ibid.*, **81**, 5750 (1959); (c) D. J. Cram, K. R. Kopecky, F. Hauck and A. Langemann, *ibid.*, **81**, 5754 (1959). Tables, compounds and runs are numbered consecutively throughout the first six papers of this series.

TABLE IX

CLEAVAGE OF OPTICALLY PURE (+)-2-METHYL-1,1,2-TRIPHENYL-1-BUTANOL

			Proton source		Base				2-Phenylbutane						
Run	St. mat. concn., *M*	Solvent	Nature	Concn., *M*	Nature	Concn., *M*	T., °C.	Tm., hr.	Yld., %	n^{25}D	α^{25}D[a]	% opt. purity[b]	Predom. steric course	% yld. dimer	Remarks
82	0.48	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	4.8	$KO(CH_2CH_2O)_2H$	0.24	140	38	66	1.4878	+14.5°	60	Ret.	19	Sealed tube
83	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	0.1	$KO(CH_2CH_2O)_2H$	.05	91	0.17	6	1.4878	+22.8	94	Ret.	1	Aliquots taken at intervals—$KO(CH_2CH_2O)_2H$ crystallized out and remained throughout run; otherwise, homogeneous
84	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	$KO(CH_2CH_2O)_2H$	.05	91	0.33	13	1.4878	+21.2	88	Ret.	2	
85	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	$KO(CH_2CH_2O)_2H$	.05	91	0.67	26	1.4878	+20.5	85	Ret.	4	
86	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	$KO(CH_2CH_2O)_2H$	.05	91	1.67	40	1.4878	+20.4	84	Ret.	7	
87	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	$KO(CH_2CH_2O)_2H$	.05	91	67	58	1.4879	+19.6	81	Ret.	15	
88	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	none	..	91	17	0	....	....	..	..	..	Optically pure st. mat. recovd.
89	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	$KO(CH_2CH_2O)_2H$	.05	91	22	68	1.4880	+19.9	82	Ret.	15	Soln. 0.10 *M* in anthracene
90	.10	$O(CH_2CH_2)_2O$	$HO(CH_2CH_2O)_2H$	.1	$LiO(CH_2CH_2O)_2H$	.05	91	15	0	....	....	..	..	..	95% recovery of starting mat.
91	.10	$O(CH_2CH_2)_2O$	$(CH_3)_3COH$	.2	$KOC(CH_3)_3$	.05	91	23	73	1.4879	+16.20	67	Ret.	4	Homogeneous, yellow
92	.10	$O(CH_2CH_2)_2O$	$(CH_3)_3COH$	.2	$NaOC(CH_3)_3$	.05	91	16	76	1.4878	+15.54	64	Ret.	10	Homogeneous, yellow
93	.10	$O(CH_2CH_2)_2O$	$(CH_3)_3COH$	.2	$LiOC(CH_3)_3$	.05	91	24	21	1.4878	+ 3.76	16	Ret.	65	Homogeneous, green, then yell.
94	.10	$O(CH_2CH_2)_2O$	$(CH_3)_3COH$	.2	$KOC(CH_3)_3$	.05	50	216	40	1.4879	+21.8	90	Ret.	3	28% st. mat. isolated, 95% opt. pure
95	.10	$O(CH_2CH_2)_2O$	$(CH_3)_3COH$	.2	$LiOC(CH_3)_3$	.05	91	4	9	1.4878	+ 3.01	12	Ret.	..	23% st. mat. isolated, 5% opt. pure
96	.10	$(CH_3)_3COH$	$(CH_3)_3COH$	..	$KOC(CH_3)_3$	.05	90	23	52	1.4878	+ 6.12	25	Ret.	..	41% yield of benzophenone
97	.56	$(CH_3)_3COH$	$(CH_3)_3COH$	..	$KOC(CH_3)_3$	.57	90	16	57	1.4879	+ 5.02	21	Ret.	..	55% yield of benzophenone
98	.82	C_2H_5OH	C_2H_5OH	..	$KOCH_2CH_3$	.82	160	20	47	1.4880	− 0.66	3	Inv.	..	....
99	1.08	CH_3OH	CH_3OH	..	$KOCH_3$	1.08	160	20	32	1.4881	− 2.93	12	Inv.	23	....
100	0.56	$O(CH_2CH_2OH)_2$	$O(CH_2CH_2OH)_2$	..	$KO(CH_2CH_2O)_2H$	0.56	155	20	36	1.4880	− 3.01	12	Inv.	18	33% yield benzhydrol
101	.10	$O(CH_2CH_2OH)_2$	$O(CH_2CH_2OH)_2$	..	$KO(CH_2CH_2O)_2H$	.05	90	42	2	1.4878	− 7.76	32	Inv.	..	....
102	.10	$O(CH_2CH_2OH)_2$	$O(CH_2CH_2OH)_2$	..	$KO(CH_2CH_2O)_2H$	.05	90	189	5	1.4878	− 8.80	36	Inv.	22	60% yield benzophenone, 6% yield of opt. pure st. mat.
103	.10	$O(CH_2CH_2OH)_2$	$O(CH_2CH_2OH)_2$	..	$KO(CH_2CH_2O)_2H$	.05	130	1	20	1.4878	− 5.84	24	Inv.	25	23% yield of opt. pure st. mat.
104	.10	$O(CH_2CH_2OH)_2$	$O(CH_2CH_2OH)_2$	..	$KO(CH_2CH_2O)_2H$	.05	130	5	32	1.4878	− 5.24	22	Inv.	32	73% yield of benzophenone
105	.10	$O(CH_2CH_2OH)_2$	$O(CH_2CH_2OH)_2$	..	$KO(CH_2CH_2O)_2H$	.05	150	3	47	1.4876	− 2.16	9	Inv.	20	68% yield of benzophenone
106	.23	C_6H_6	none	..	LiC_6H_5	.23	60	10	..	....	....	..	..	35	24% yield of racemic st. mat.
107	.63	$HOCH_2CH_2OH$	$HOCH_2CH_2OH$	..	$KOCH_2CH_2OH$	.9	150	4	34	1.4881	− 2.51	10	Inv.	37	Heterogeneous, 23% st. mat., 11% opt. pure

[a] *l* 1 dm., neat. [b] Optically pure 2-phenylbutane has α^{25}D ±24.3° (*l* 1 dm., neat).

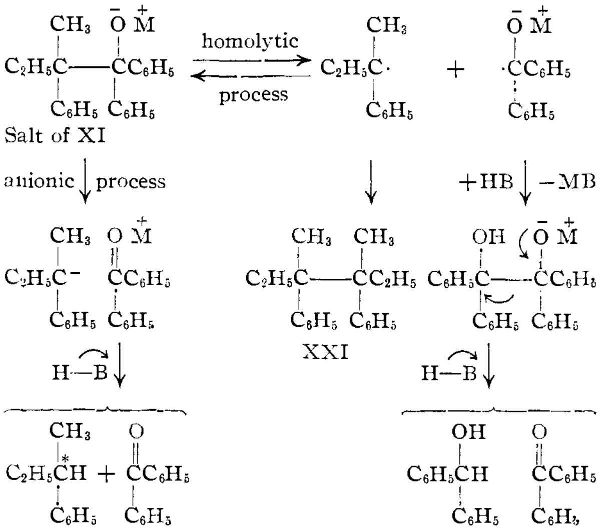
same solvent and at about the same temperature to give I, but in which the substituents attached to the leaving groups were other than phenyl. (1) In the early part of run 82 the reaction turned green, then yellow, and then the color disappeared; in runs with other systems,[3b,3c] no color changes of this sort were observed. (2) Other systems gave I with higher retention of configuration. (3) Unlike any other systems, XI produced along with I a higher-boiling hydrocarbon of molecular formula $C_{20}H_{26}$, which partially crystallized when allowed to stand. These differences suggested that the cleavage of XI took a somewhat different course from that of other systems, and therefore the behavior of XI was examined in some detail.

In run 106, XI was converted in dry benzene with phenyllithium to its lithium salt at 25°, and the solution was then heated at 60° for 10 hours. No proton donor was present in the reaction medium. A 35% yield of $C_{20}H_{26}$ hydrocarbon (optically inactive) was isolated from the reaction mixture as well as 24% of the starting material. Although optically pure XI was initially employed, *the material recovered was completely racemic.* Since the asymmetric carbon of XI is quaternary, the compound can racemize only by breaking and reforming a carbon–carbon bond.

From the $C_{20}H_{26}$ hydrocarbon mixture was isolated a crystalline component, which was demonstrated to be identical with the sample of 3,4-dimethyl-3,4-diphenylhexane (XXI) prepared by Eliel[4] by decomposition of acetyl peroxide in optically active 2-phenylbutane. Thus the $C_{20}H_{26}$ hydrocarbon was probably a mixture of racemic and *meso*-XXI, and one of these isomers crystallized.

These facts indicate that salts of XI undergo both a homolytic and heterolytic cleavage in competition with one another, and that the homolytic cleavage is reversible and leads to racemic starting material through the inability of the 2-phenyl-2-butyl radical to maintain its configuration.[5] The $C_{20}H_{26}$ hydrocarbon comes from the combination of two 2-phenyl-2-butyl radicals, which in other instances[5] have given a mixture of both racemic and *meso* material. Such a scheme leaves unexplained the fate of those benzophenone ketyls (radical anions) which do not recombine with 2-phenyl-2-butyl radicals to give XI.

The results of the two following experiments indicate that these radical anions combine with one another to give tetraphenylethylene glycol, which itself then undergoes anionic cleavage to give diphenyl ketone and benzhydrol. In the first experiment, the lithium salt of XI was heated in dioxane–*t*-butyl alcohol, and the products were 25% 2-phenylbutane, 61% $C_{20}H_{26}$ hydrocarbon, 66% benzophenone and 27% benzhydrol. In the second experiment it was demonstrated that tetraphenylethylene glycol cleaves under the same conditions, presumably by an anionic process, to give benzhydrol and benzophenone. In a control experiment (run 88), optically pure XI was shown to persist under similar conditions but in the absence of base. The reaction scheme is formulated.



Salt of XI

XXI

In runs 83–87 a study was made of the yields of 2-phenylbutane and of $C_{20}H_{26}$ hydrocarbon, and of the optical purity of 2-phenylbutane produced as a function of time when the cleavage was carried out in dioxane (91°, reflux temperature in Mexico City) with potassium diethylene glycoxide as base. In Fig. 1 these results are plotted. Extrapolation to time = zero of the curve which describes the change in optical purity of 2-phenylbutane with time gives a value of 99–100% optical purity for this hydrocarbon. Clearly the anionic cleavage reaction is essentially completely stereospecific, and the electrophilic substitution reaction occurs with complete retention of configuration under these conditions. The departure from optical purity of 2-phenylbutane produced at the longer times is due to racemization of the starting material by reversible homolytic cleavage. It was demonstrated earlier[4] that the 2-phenyl-2-butyl radical does not abstract hydrogen from 2-phenylbutane at a rate which can compete with that of dimerization of the radical.

When the reaction was allowed to go to completion (run 87), the 2-phenylbutane produced was 81% optically pure, which indicates that 19% of the 2-phenylbutane must have come from starting material racemized through the homolytic cleavage reaction. Since the yields of $C_{20}H_{26}$ hydrocarbon (15%) and of racemic 2-phenylbutane (0.19 × 58% = 11%) are quite close together, the rates of combination of two 2-phenyl-2-butyl radicals must have been about the same as the rate of recombination of 2-phenyl-2-butyl radicals with benzophenone radical anions to give racemic XI. The ratio of rates of heterolytic and homolytic cleavage is approximately equal to 1.8 [47% (yield of optically pure 2-phenylbutane)/11% (yield of racemic 2-phenylbutane) + 15% (yield of $C_{20}H_{26}$ hydrocarbon)] for run 87.

In run 89, an attempt was made to eradicate the recombination of radicals to give racemic XI by

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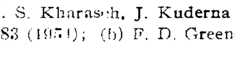
(4) E. L. Eliel, P. H. Wilken, F. T. Fang and S. H. Wilen, THIS JOURNAL, **80**, 3303 (1958). The authors wish to thank Dr. Eliel for a sample of crystalline *meso*-XXI.

(5) A number of investigators have decomposed acyl peroxides of the type  and have obtained both racemic and optically active products as a result of homolytic cleavage reactions: (a) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954); (b) F. D. Greene, THIS JOURNAL, **77**, 4869 (1955).

capturing the 2-phenylbutyl radical with added anthracene.[6] The similarity between the results of this run and run 87 indicate that neither of the two kinds of radicals were trapped by anthracene.

Run 90 was conducted under the same conditions as run 87 except that lithium was substituted for potassium. No reaction occurred, and this result provides an interesting example of the difference in reactivity of lithium and potassium salts.

In runs 91, 92 and 93, the patterns of products are compared in three parallel experiments in which potassium, sodium and lithium *t*-butoxides are used as bases, and dioxane is employed as solvent. If it is assumed that had the homolytic reaction been absent the 2-phenylbutane produced would have been about 95% optically pure (see discussion below of results of run 94), then $k_{\text{heterolytic}}/k_{\text{homolytic}}$ can be estimated for the three runs as

Run	Salt	$k_{\text{heterolytic}}/k_{\text{homolytic}}$
91	K	2.2
92	Na	1.6
93	Li	0.05

The striking difference in behavior of the potassium and sodium salts on one hand and the lithium salt on the other can be explained as follows. The oxygen–metal bond in salts of XI probably has degrees of covalent character that varies with the metal in the order, Li > Na > K. In the heterolytic cleavage, the O–M bond as well as the C–C bond is completely broken, whereas in the homolytic cleavage, only the C–C bond is broken. Thus the more covalent the O–M bond, the slower the heterolytic cleavage is expected to be relative to that of the homolytic variety.

In run 94 with potassium salt and run 95 with lithium salt, the reactions (in dioxane) were allowed to go only about three-quarters of the way toward completion, and starting material was then isolated. In run 94, 28% of starting material was recovered which was 95% optically pure, and the 2-phenylbutane produced was 90% optically pure. Clearly, the stereospecificity in the heterolytic cleavage must have been between 90 and 95%. In run 95, 23% of the starting material was recovered, and this material was only 5% optically pure. The 2-phenylbutane isolated was only 12% optically pure. These runs were both conducted in dioxane with *t*-butoxide as base.

In runs 96 and 97, the cleavages were carried out in *t*-butyl alcohol as solvent with potassium *t*-butoxide as base. Although the concentrations of base differed in these experiments by a factor of 10, the 2-phenylbutane produced showed about the same degree of optical purity, 21 and 25% in the two runs. These reactions were run to completion, and were far less stereospecific than the comparable run (94) in dioxane, which if carried to completion would have given 2-phenylbutane at least 80% optically pure. It seems probable that the relatively low stereospecificity in runs 96 and 97 is the result of prior racemization of starting material by the reversible homolytic cleavage reaction. The difference in temperatures (40°) might account for the difference in stereospecificity of run 94 on the one hand and runs 96 and 97 on the other. Thus $k_{\text{heterolytic}}/k_{\text{homolytic}}$ probably decreases in value with increased temperature.

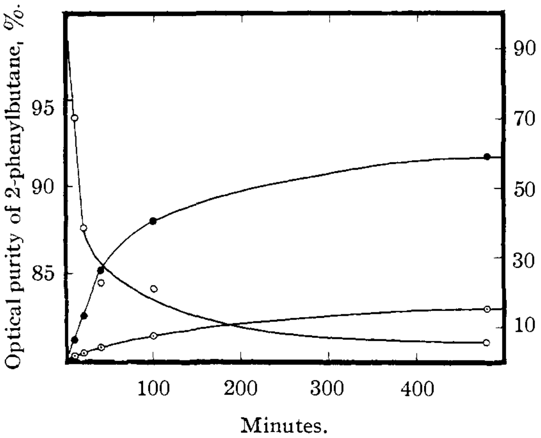


Fig. 1.—Results of cleavage of (+)-XI in dioxane–potassium diethylene glycoxide at 91°: curve O, plot of optical purity (lefthand vertical axis) of 2-phenylbutane *vs.* time; curve ●, plot of yield (right-hand vertical axis) of 2-phenylbutane *vs.* time; curve ⊙, plot of yield (right-hand vertical axis) of $C_{20}H_{26}$ hydrocarbon *vs.* time.

In runs 97–100, the effect of changes in solvent on the steric course of the electrophilic substitution reaction is assessed. Retention of configuration decreases and inversion increases as the solvent is successively changed from *t*-butyl alcohol to ethanol to methanol to diethylene glycol, as was observed earlier with the 3,4-dimethyl-4-phenyl-3-hexanol system.[3b]

In run 102 in diethylene glycol (90°), a 5% yield of 2-phenylbutane of predominantly inverted configuration (36% optically pure) was obtained along with a 22% yield of $C_{20}H_{26}$ hydrocarbon and 6% of optically pure starting material. The higher yield of the higher molecular weight hydrocarbon indicates that homolytic is faster than heterolytic cleavage in this solvent. However, unlike the results in other solvent systems, recovered starting material was optically pure, a fact which indicates that the reverse of the homolytic cleavage reaction was very slow compared to dimerization or other reactions of the 2-phenyl-2-butyl radical in this experiment. The same conclusion can be drawn from the results of run 103, which was conducted under the same conditions as 102 except that the temperature was raised to 130°. In this case, 23% of optically pure starting material was recovered. Thus up to 130°, racemization of the starting material does not play an important role in determining the optical purity of the 2-phenylbutane produced when diethylene glycol is solvent and potassium diethylene glycoxide is base.

In Table X are recorded the changes in the ratios of yields of 2-phenylbutane and $C_{20}H_{26}$ hydrocarbon, and the changes in optical purity of the former compound with changes in temperature for runs 102, 104 and 105. For a difference of 60° in temperature, the ratios of yields vary tenfold, and the optical purity of 2-phenylbutane samples differ by as much as a factor of 4. At higher temperatures, the yields of 2-phenylbutane increase at the expense

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[6] See A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956).

of those of the $C_{20}H_{26}$ hydrocarbon, and at the same time, the optical purity of the 2-phenylbutane decreases. In a number of other systems, smaller changes in optical purity were observed with changes in temperature. For instance, when 2,3-diphenyl-3-methyl-2-pentanol was cleaved in diethylene glycol at 150 and 180°,[7] inverted 2-phenylbutane of 60 and 54% optical purity was obtained, respectively.

Table X

Effect of Temperature on Course of Cleavage of Optically Pure (+)-2-Methyl-1,1,2-triphenyl-1-butanol in Diethylene Glycol 0.05 M in Potassium Diethylene Glycoxide

Run	Temp., °C.	Yld. 2-phenylbutane / Yld. $C_{20}H_{26}$ hydroc.	% optical purity 2-phenylbutane
102	90	0.23	36
104	130	1.0	22
105	150	2.3	9

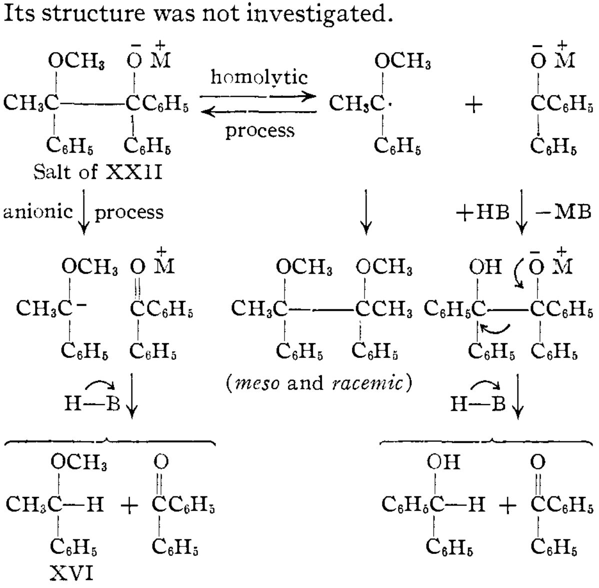
These results strongly suggest that the 2-phenyl-2-butyl radical produces racemic 2-phenylbutane by abstracting a hydrogen atom from the α-carbon of the conjugate base of diethylene glycol. This reaction competes with that of dimerization of the radical, and at higher temperatures, substitution of the radical increases at the expense of the dimerization. Thus as the temperature increases, the optically active 2-phenylbutane produced by anionic cleavage is diluted with racemic 2-phenylbutane produced by the hydrogen-atom abstraction process, and the yield of dimeric hydrocarbon is reduced accordingly.

The same hydrogen-abstraction process probably also occurs in runs 83–87, but at a very low rate due to the low temperature (91°). Possibly the relatively low rotation of 2-phenylbutane (60% optically pure) observed in run 82 as compared to run 87 (81% optically pure) is partially due to the direct production of racemic 2-phenylbutane from 2-phenyl-2-butyl radicals, a process which might be favored at the higher temperature (140°) and base concentration of run 82.

In run 107, carried out in ethylene glycol at 150°, a 34% yield of 10% optically pure and inverted 2-phenylbutane, a 37% yield of $C_{20}H_{26}$ hydrocarbon, and a 23% recovery of 11% optically pure starting material was obtained. The high temperature and possibly the heterogeneous character of this reaction probably accounts for the high rate of racemization of starting material in this run (compare with runs 102 and 103).

In those runs of Table IX in which the homolytic reaction occurred at a high rate, a yellow to green color developed which reached a maximum of intensity and then faded. This color is attributed to a combination of the green color of the benzophenone radical anion,[8] and possibly the yellow color of the 2-phenyl-2-butyl radical, whose concentrations must reach a maximum and then decline.

Cleavage Reactions of Racemic 1,1,2-Triphenyl-2-methoxy-1-propanol (XXII).—In an attempt to see how general the homolytic cleavage is of systems that can produce the ketyl of benzophenone as an initial product, racemic 1,1,2-triphenyl-2-methoxy-1-propanol (XXII) was prepared and heated with lithium t-butoxide in dioxane at 140°. The reaction mixture immediately became intense green, and this color faded slowly into a light yellow. The products of this reaction indicate that both anionic and radical cleavage reactions occurred, as formulated. The ionic cleavage gave benzophenone and 1-methoxy-1-phenylethane (XVI), whereas the radical cleavage gave a mixture of *meso-* and *racemic* 2,3-dimethoxy-2,3-diphenylbutane[9] by dimerization of the 1-phenyl-1-methoxy-1-ethyl radical. The ketyl of benzophenone probably reversibly dimerized to produce the dianion of tetraphenylethylene glycol, which cleaved by an ionic process to give the observed products, benzophenone and benzhydrol (see formulation). Similar dimerizations[10] and cleavages[11] have been observed in other investigations. An anomalous ketone was also isolated from the reaction mixture. The molecular formula of this compound ($C_{22}H_{20}O$) is equal to that of XXII minus one mole of water. Its structure was not investigated.



Cleavage Reactions of Optically Pure (+)-1,1-Diphenyl-2-cyclohexyl-2-methyl-1-butanol (XXIII).—An attempt was made to study the anionic cleavage of system XXIII, in which benzophenone is the leaving group, and in which the 2-cyclohexyl-2-butyl anion is substituted with a proton to give 2-cyclohexylbutane. In both ethylene glycol–potassium ethylene glycoxide, and in t-butyl alcohol–potassium t-butoxide, completely racemic 2-cyclohexylbutane was produced. The green color of the reactions coupled with the nature of the products indicate that homolytic cleavage occurred, and probably the 2-cyclohexylbutane arose by a process which involved the 2-cyclohexyl-2-butyl radical as an intermediate. The extreme instability of the 2-cyclohexyl-2-butyl anion accounts for the absence of a competitive anionic cleavage in this system.

No product was isolated which corresponded to the dimer of 2-cyclohexyl-2-butyl radical. However, olefinic hydrocarbon was demonstrated to be

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(7) See runs 78 and 79, Table VI of ref. 3c.

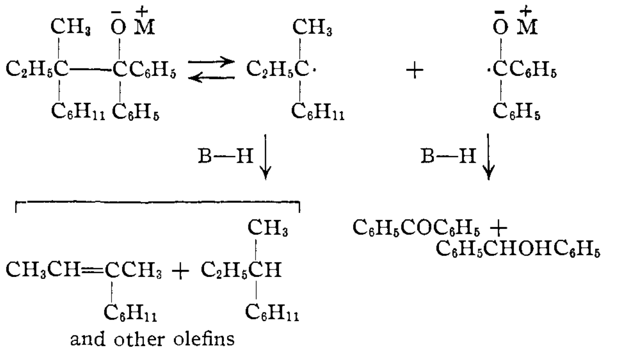
(8) W. E. Bachmann, This Journal, **55**, 1179 (1933).

(9) D. J. Cram and K. R. Kopecky, *ibid.*, **81**, 2748 (1959).

(10) S. Sugden, *Trans. Faraday Soc.*, **30**, 18 (1934).

(11) W. D. Cohen and J. Boseken, *Rec. trav. chim.*, **38**, 113 (1919).

produced, which suggests that rather than adding to one another, these radicals disproportionate, particularly in *t*-butyl alcohol, which itself is a poor source of hydrogen atoms. The suggested reaction scheme is



Experimental

Starting Materials.—The preparation and properties of optically pure (+)-2-methyl-1,1,2-triphenyl-1-butanol (XI) have been previously reported.[3a] The material employed in this paper had $[\alpha]^{25}D$ +31.6° (*c* 7, benzene). The other two alcohols, racemic 1,1,2-triphenyl-2-methoxy-1-propanol (XXII) and optically pure (+)-1,1-diphenyl-2-cyclohexyl-2-methyl-1-butanol (XXIII), are reported below for the first time.

Alcohol XXII was prepared as follows. To a solution of phenylmagnesium bromide (made from 17 g. of bromobenzene and 2.6 g. of magnesium) in 200 ml. of ether was added dropwise 10 g. of racemic methyl 2-methoxy-2-phenylpropionate.[9] The resulting mixture was held at reflux temperature for 3 hours, and then poured into a mixture of ice and very dilute sulfuric acid. The ethereal layer was washed with water and dilute sodium carbonate solution, dried and evaporated. The residual oil was dissolved in 50 ml. of pure pentane, and the resulting solution was cooled to 0° for 3 days. The white cubes of XXII that separated were collected; weight 12.0 g. (70% yield), m.p. 92–94°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.02; H, 6.92. Found: C, 83.17; H, 6.98.

Alcohol XXIII was prepared as follows. To a 100 ml. of ethereal solution of phenyllithium (from 0.50 g. of lithium and 5.12 g. of bromobenzene) was added a solution of 2.7 g. of optically pure (+)-methyl 2-cyclohexyl-2-methylbutanoate[3a] in 25 ml. of dry ether. The resulting mixture was held at reflux for 14 hours and then poured onto a mixture of ice and saturated ammonium chloride solution. The ethereal layer was washed with water, with sodium carbonate solution, was dried, and concentrated. The residual oil was chromatographed on 250 g. of neutral, activated alumina. Benzene, bromobenzene and biphenyl were eluted with one liter of 5% ether–pentane (carefully purified). The desired (+)-1,1-diphenyl-2-cyclohexyl-2-methyl-1-butanol was eluted with 50% ether–pentane, and was crystallized from pentane as heavy cubes, weight 3.7 g. (87% yield), m.p. 46–47°, $[\alpha]^{23}D$ +14.3° (*c* 4, chloroform).

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.68; H, 9.37. Found: C, 85.79; H, 9.66.

Purification of Solvents.—The solvents employed in the cleavage reactions were all purified by the methods reported earlier.[3b,3c] Before use, they were all saturated with nitrogen.

Cleavage Reactions.—The cleavage reactions were carried out in much the same ways as have been reported in earlier papers of this series.[3b,3c] Those procedures which deviated from the general methods are indicated as follows.

Run 82.—This reaction was carried out in a sealed tube.

Runs 83–87.—In these runs, equal aliquots were taken from the reaction mixture, and the products isolated at the times indicated in Table IX. The reaction mixture turned a brilliant green which faded to a light yellow as the reaction proceeded. The reaction mixture was saturated with potassium diethylene glycoxide throughout the run, which crystallized out before the starting alcohol was added, and remained as a second phase during the reaction.

Run 88.—This run was carried out exactly as in runs 83–87 except the base was left out of the reaction mixture. Starting material was recovered in 96% yield, and possessed the same rotation, $[\alpha]^{25}D$ +31.4° (*c* 7, benzene), as starting material.

Run 89.—The reaction solution was 0.1 *M* in anthracene.

Run 90.—A 95% recovery of starting material was obtained. The rotation of this material was not determined.

Runs 91–93.—These runs were carried out under identical conditions except for reaction times. The reactions were homogeneous. In runs 91 and 92 a yellow-green color, and in run 93, a brilliant green color developed during the early part of the reaction.

Run 94.—The procedure is illustrative, and will be given in its entirety. Potassium metal, 0.093 g., was allowed to react with 3 ml. of *t*-butyl alcohol, and the resulting mixture was concentrated until the total weight was 0.80 g. This material was dissolved in 47 ml. of pure dioxane saturated with nitrogen and containing 1.5 g. of alcohol XI. The resulting solution was heated in a dry nitrogen atmosphere for 216 hours, cooled, and shaken with a mixture of 200 ml. of pure pentane and 200 ml. of water. The water layer was washed with pure pentane, and the combined pentane layers were washed with three 100-ml. portions of water. The organic layer was dried, the solvent was evaporated through a 2-foot Vigreux column, and the residual oil was chromatographed on 100 g. of basic alumina. The hydrocarbon product was washed from the column with pure pentane, and the eluent was evaporated through a 2-foot Vigreux column. The residual oil was distilled at 25 mm. pressure and a pot temperature of 80°. The distillate was again distilled to give 0.255 g. of 2-phenylbutane, 40% yield, $n^{25}D$ 1.4879, $\alpha^{25}D$ +21.8° (*l* 1 dm., neat). The residual oil from the first distillation was distilled at 1 mm. and a pot temperature of 150° to give 0.020 g. of $C_{20}H_{26}$ hydrocarbon, 3% yield.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.12; H, 9.90.

The chromatograph column was eluted with ether, and solvent was evaporated from the eluate. The residual oil was reduced with lithium aluminum hydride in the usual way to convert the benzophenone present to benzhydrol, which is chromatographically easier to separate from XI. The resulting material was chromatographed on 60 g. of activity II neutral alumina.[12] Starting alcohol (XI) was eluted from the column with 9-to-1 pentane–ether. Evaporation of the eluate gave an oil which was freed from solvent by heating it to 60° as a film at 0.1 mm. pressure, weight 0.415 g., $[\alpha]^{23}D$ +28.7° (*c* 7, benzene).

Anal. Calcd. for $C_{22}H_{24}O$: C, 87.30; H, 7.65. Found: C, 87.37; H, 7.90.

Run 95.—The procedure was the same as in run 94.

Run 96.—The same procedure was employed here as in run 94 except that the lithium aluminum hydride step was omitted, and benzophenone was isolated as in run 97.

Run 97.—In this run, benzophenone was isolated from a 9-to-1 pentane–ether eluate of the chromatogram used to separate hydrocarbon from oxygen-containing compounds. The material crystallized from pentane, m.p. 48–50°, undepressed by admixture with authentic benzophenone.

The $C_{20}H_{26}$ hydrocarbon samples obtained in run 93 and this run were combined to give material, $[\alpha]^{25}D$ 0.00 (*c* 10, benzene).

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.10; H, 10.02.

This material was crystallized and recrystallized five times from methanol, m.p. 98–99°, undepressed by admixture with 3,4-dimethyl-3,4-diphenylhexane.[4]

Run 98.—This reaction was run in a heavy-walled sealed tube.

Run 99.—This reaction was run in a heavy-walled sealed tube. The $C_{20}H_{26}$ hydrocarbon had $[\alpha]^{25}D$ 0.00° (*c* 20, benzene). A micro-Rast molecular weight was taken on this material; calcd. for $C_{20}H_{26}$ 266, found 290. When allowed to stand, this material crystallized, and two recrystallizations of the material from pentane gave colorless plates, m.p. 92–95°. This material was not further purified.

Run 100.—In this run, benzhydrol was washed with 50% ether–50% methanol from the chromatogram used to separate hydrocarbon from oxygen-containing materials. The

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[12] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

material was crystallized from pentane–ether, m.p. 66–68°, undepressed by admixture with authentic material.

Runs 101, 104 and 105.—These reactions were carried out in the usual way. Benzophenone was isolated as in run 97. The samples of $C_{20}H_{26}$ hydrocarbon were combined, and crystallized and recrystallized seven times in hot methanol, m.p. 98–98.5°, undepressed by admixture with an authentic sample of 3,4-dimethyl-3,4-diphenylhexane (m.p. 98–99°).[4]

Run 102.—The starting material and benzophenone were obtained from the reaction mixture by careful chromatography on activity *II* neutral alumina.[12] Benzophenone was eluted with 12-to-1 pentane–ether, and alcohol XI with 7-to-1 pentane–ether. The infrared spectrum of alcohol XI was identical in detail with that of authentic material.

Run 103.—Starting material was isolated as in run 94.

Run 106.—Excess lithium metal was allowed to react with bromobenzene in ether under an atmosphere of pure nitrogen. The resulting mixture was filtered under nitrogen, and the ether was replaced with dry benzene. An aliquot of the resulting solution was titrated[13] and found to be 1.22 *N* in phenyllithium. To a solution of 1.00 g. (0.00317 mole) of alcohol XI in 10 ml. of dry benzene was added 2.60 ml. (0.00315 mole) of phenyllithium solution. The resulting green solution was held at reflux under dry nitrogen for 10 hours, after which the mixture had become more brown. The reaction mixture was cooled, shaken with water, and the organic layer was dried and evaporated. The residual oil was chromatographed on 50 g. of neutral activity II alumina.[12] The column was washed with pentane to give $C_{20}H_{26}$ hydrocarbon in 35% yield.

This material was recrystallized from pentane three times to give compound IV, m.p. 97–98°, undepressed by admixture with authentic material.[4]

Starting material and benzophenone were washed from the column with 4:1 pentane–ether, and the mixture was treated with lithium aluminum hydride. The resulting mixture was separated by chromatography to give 0.24 g. (24% yield) of XI as a colorless oil, $n^{25}\mathrm{D}$ 1.6056, $\alpha^{25}\mathrm{D}$ 0.00 (*c* 4 in C_6H_6). The infrared spectrum of this material was identical to that of the starting material.

Anal. Calcd. for $C_{23}H_{24}O$: C, 87.30; H, 7.65. Found: C, 87.30; H, 7.60.

Run 107.—This run was carried out in a sealed tube under nitrogen, and was heterogeneous. Starting material was isolated as in run 94.

Cleavage of Racemic 2-Methyl-1,1,2-triphenyl-1-butanol (XI) in *t*-Butyl Alcohol-Lithium *t*-Butoxide for Product Analysis.—A solution of 0.063 g. of lithium metal in 2.8 g. of *t*-butyl alcohol was added to a solution of 6.0 g. of racemic XI dissolved in 186 ml. of dioxane saturated with dry nitrogen. The resulting solution was heated to 91° for 42 hours under nitrogen, cooled, and shaken with 500 ml. of pure pentane and 500 ml. of water. The water layer was washed with 200 ml. of pentane, and the combined pentane layers were washed with five 200-ml. portions of water. The organic layer was dried, and the solvent was evaporated through a 2-foot Vigreux column to give an oil, which was chromatographed on 200 g. of basic alumina. The hydrocarbon fraction was washed from the column with pure pentane to give 0.630 g. of 2-phenylbutane (25% yield), $n^{25}\mathrm{D}$ 1.4880, and 1.56 g. of $C_{20}H_{26}$ hydrocarbon (61% yield). This latter material was crystallized from pentane to give 0.85 g. of solid as first crop, m.p. 91–96°, and 0.70 g. of second crop, m.p. 50–60°. Benzophenone was washed from the chromatograph column with 4:1 pentane–ether, and was crystallized from methanol to give 2.05 g. of ketone (66% yield), m.p. 48–50°, undepressed by admixture with an authentic sample. Benzhydrol was washed from the column with 1-to-1 ether–methanol, and was crystallized from ether–pentane, weight 0.80 g. (27% yield), m.p. 67–68°, undepressed by admixture with an authentic sample.

Cleavage of Benzpinacol.—Potassium metal (0.093 g.) dissolved in 0.70 g. of *t*-butyl alcohol was added to a solution of 2.48 g. of benzpinacol in 94 ml. of dioxane. The mixture was held at 91° under pure nitrogen for 42 hours, and the products isolated in the usual way. The mixture of products was chromatographed on 100 g. of basic alumina. No material was washed from the column with pentane. Benzophenone was eluted with 4:1 pentane–ether and was crystallized from pentane to give 1.06 g. of material (71% yield), m.p. 48–50°, undepressed by admixture with an authentic sample. Benzhydrol was washed from the column with 1-to-1 ether–methanol, and was crystallized from ether–pentane to give 0.85 g. (56% yield) of benzhydrol, m.p. 67–68°, undepressed by admixture with an authentic sample.

Cleavage of Racemic 1,1,2-Triphenyl-2-methoxy-1-propanol (XXII).—To a solution of lithium *t*-butoxide (prepared from 0.049 g. of lithium) in 20 ml. of dioxane (saturated with pure nitrogen) was added 2.0 g. of alcohol XXII. The reaction mixture was heated in a Wood metal-bath to 80° under pure nitrogen, and the reaction flask (pressure bottle) was closed. The flask was heated at the rate of one degree a minute until 140° was reached. At 100° the reaction mixture became faint green, and the color deepened as the temperature was increased. After 3.5 hours at 140° the dark green had faded to a light yellow. The reaction mixture was cooled, and shaken with a mixture of 100 ml. of pure pentane and 100 ml. of water. The water layer was washed with 50 ml. of pentane, and the combined organic layers were washed with four 50-ml. portions of water. The organic layer was dried and evaporated to about 5 ml. When cooled, this solution deposited 0.20 g. (23% yield) of *meso*-2,3-dimethoxy-2,3-diphenylbutane, m.p. 171–173°, undepressed upon admixture with an authentic sample of the material.[9]

The filtrate was adsorbed on 2 × 30 cm. column of neutral, activated alumina. The chromatograph column was eluted with 1.5 liters of pure pentane, and the elute when concentrated gave a mixture of oil (odor of 1-methoxy-1-phenylethane (XVI)) and fine crystals. The oil was pipetted from the crystals and flash distilled at *ca.* 40 mm. pressure and a pot temperature of 80° to give 0.26 g. (3%) of a colorless oil, $n^{25}\mathrm{D}$ 1.4820. The solid was recrystallized from pentane to give 0.19 g. of (22%) *dl*-2,3-dimethoxy-2,3-diphenyl-butane, m.p. 108–110°, undepressed upon admixture with an authentic sample of the material.[9]

The chromatograph column was eluted with 10-to-1 pentane–ether (1.7 liters), and the eluate when concentrated gave an oil which crystallized from pentane to give 0.56 g. (45% yield) of benzophenone, m.p. 47–48°, undepressed by admixture with an authentic sample.

Elution of the column with ether gave material which crystallized from pentane, weight 0.20 g., m.p. 97.5–98° (white needles), strong band at 1657 cm.$^{-1}$ in the infrared, no band in the O–H stretching region.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.72. Found: C, 88.25; H, 6.75.

The column was then eluted with 250 ml. of methanol. The eluate when concentrated gave an oil which was recrystallized from ether–pentane to give 0.30 g. (25% yield) of benzhydrol, m.p. 67–69°, undepressed by admixture with an authentic sample.

Cleavage of (+)-1,1-Diphenyl-2-cyclohexyl-2-methyl-1-butanol (XXIII).—This substance was cleaved in both ethylene glycol and in *t*-butyl alcohol. The procedures are summarized.

In Ethylene Glycol.—A solution of potassium ethylene glycoxide was prepared from 0.16 g. (0.0041 g. atom) of potassium (*via* potassium *t*-butoxide[3b]) and 3.3 g. of ethylene glycol saturated with nitrogen. To this solution was added 1.5 g. (0.0047 mole) of (+)-XXIII, and the resulting mixture was heated to 215° under nitrogen for 40 hours. Two phases were present throughout the reaction.

The products were isolated as in run 100. The hydrocarbon fraction distilled readily at 25 mm. and a pot temperature of 90° to give 0.53 g. (79% yield) of 2-cyclohexylbutane contaminated with a small amount of olefin, $n^{25}\mathrm{D}$ 1.4452. Olefin was removed by a procedure recorded previously[3a,3c] to give 0.35 g. of 2-cyclohexylbutane,[3a] $n^{25}\mathrm{D}$ 1.4442, $\alpha^{25}\mathrm{D}$ 0.00° (neat, *l* 1 dm.).

Elution of the chromatograph column with pure ether gave no material. Elution with methanol gave 0.7 g. of benzhydrol, m.p. 65–66°, undepressed by admixture with an authentic sample. The absence of benzophenone in this run is probably due to its reduction by base and ethylene glycol to benzhydrol.

In *t*-Butyl Alcohol.—To a solution of 0.2 g. (0.0051 g. atom) of potassium dissolved in 4.4 ml. of *t*-butyl alcohol (saturated with pure nitrogen) was added 2.0 g. (0.0062 mole) of (+)-XXIII. The resulting solution was sealed in a heavy glass tube under nitrogen, and was heated to 150° in a Woods metal-bath for 23 hours. The reaction mixture be-

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(13) G. Wittig and G. Harborth, *Ber.*, **77**, 315 (1944).

came a bright green, which soon faded to a greenish-brown. The products were isolated as in other cases. The hydrocarbon fraction from the chromatograph column readily distilled to give 0.48 g. (55% yield) of 2-cyclohexylbutane[3a] heavily contaminated with olefin, $n^{25}D$ 1.4503. After olefin was removed,[3b,3c] the product weighed 0.095 g., $n^{25}D$ 1.4440, $\alpha^{24}D$ 0.00° (l 1 dm., neat).

Elution of the chromatograph column with 1-to-1 ether-pentane gave an oil which was treated with 2,4-dinitrophenylhydrazine reagent to give orange crystals. Two recrystallizations of this material from ethanol gave 0.09 g. of the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 237–239°, undepressed by admixture with an authentic sample. A second hydrazone of a higher molecular weight ketone was also isolated, but was not identified.

Elution of the chromatograph column with ether gave 0.25 g. (25% yield) of benzhydrol, m.p. 64–65°, undepressed by admixture with an authentic sample.

LOS ANGELES 24, CALIF.

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

Electrophilic Substitution at Saturated Carbon. V. Starting States and Intermediates

BY DONALD J. CRAM, FRED HAUCK, KARL R. KOPECKY AND W. DAVID NIELSEN

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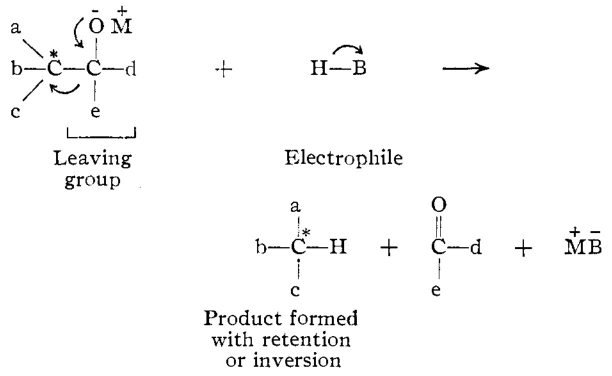
The effect of variation of the configuration of the leaving group in electrophilic substitution at saturated carbon has been investigated. In base-catalyzed cleavage reactions of optically pure *threo*- and *erythro*-1,2-diphenyl-2-methyl-1-butanol to give 2-phenylbutane, the degree of stereospecificity was essentially the same for both diastereomers in both dioxane (about 94% predominating retention) and diethylene glycol (48% predominating inversion of configuration). The steric course of electrophilic substitution in the cleavage of optically pure diastereomers of 2,3-diphenyl-3-methoxy-2-butanol to give 1-methoxy-1-phenylethane in the above solvents was also shown to be independent of the *configuration of the leaving group*. This result indicates that intermediates common to both diastereomers intervene in both the retention and inversion mechanisms. Other support for this conclusion is found in the following facts. (1) In retention solvents, the steric course of electrophilic substitution is independent of the acidity of the electrophile over a range of about 14 pK_a units. (2) In retention solvents, the steric course of the reaction is insensitive to the concentration of electrophile over concentrations that differ by a factor of 130. (3) In extreme retention and extreme inversion solvents, the steric course of the reaction depends only secondarily on the structure of the leaving group. The effect of both the nature and concentration of metal cation on the steric course of electrophilic substitution has been studied in four systems. The steric course of the reaction was independent of the concentration of the metal cation in all solvents studied. Lithium salts underwent cleavage reactions slower than potassium salts in all types of solvents. In extreme retention solvents, lithium salts gave higher retention than potassium salts. In extreme inversion solvents, with some leaving groups, both kinds of salts gave the same results. With other leaving groups, potassium salts gave higher inversion than lithium. In intermediate solvents, lithium salts gave higher inversion than potassium salts. In intermediate solvents, the systems with the least basic leaving groups gave the least retention and the highest inversion. These results provide evidence for two species in equilibrium with each other, both of which undergo electrophilic substitution. In non-dissociating solvents, intimate ion pairs cleave to give product of retained configuration. In dissociating solvents, solvent-separated ion-pairs give product of inverted configuration.

The base-catalyzed cleavage of a number of systems which conform to the general scheme indicated has been studied, and the results have been reported in previous papers of this study.[2] In the course of these reactions, electrophilic substitution occurs at the asymmetric carbon of the starting material, the steric course of which seems to be primarily controlled by the dissociating power of the solvent. Variation of the substituents (d and e) attached to the leaving group, and of the acidity and concentration of the electrophile (HB) were examined (the latter only in retention solvents), and were found to play only a secondary role in determining the steric course of the reaction.



The present study is concerned with the effects of changes in *configuration and basicity of the leaving group*, and changes in the character and concentration of the metal cation upon the steric course of the electrophilic substitution reaction.

The absolute configurations of all starting materials and products in the reactions studied have been reported in other papers, as have the rotations of optically pure materials.[3] Only optically pure starting materials were employed in these investigations.

Results

Table X records the results of cleavages of optically pure diastereomers of VI and XIV in dioxane with potassium *t*-butoxide as base (runs 108, 109, 112, 113), the former in ethylene glycol with potassium ethylene glycoxide as base (runs 110 and 111), and the latter in diethylene glycol with potassium diethylene glycoxide as base (runs 114 and 115). System VI is a secondary alcohol, and in runs 110 and 111, a possibility exists that some equilibration

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(1) This work was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to donors of said fund.

(2) (a) D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, THIS JOURNAL, **81**, 5740 (1959); (b) D. J. Cram, A. Langemann and F. Hauck, *ibid.*, **81**, 5750 (1959); (c) D. J. Cram, K. R. Kopecky, F. Hauck and A. Langemann, *ibid.*, **81**, 5754 (1959); (d) D. J. Cram, A. Langemann, W. Lwowski and K. R. Kopecky, *ibid.*, **81**, 5760 (1959). Tables, compounds and runs are numbered consecutively throughout the first six papers of this series.

(3) See ref. 2c for a summary of references and for data that demonstrate the relative configurations of starting materials and products. Rotations of optically pure starting materials are found in reference 2b.