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

Electrophilic Substitution at Saturated Carbon. VII. Steric Course of Reactions that Involve Breaking Carbon–Oxygen Bonds[1]

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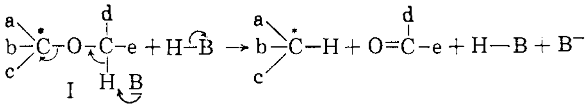
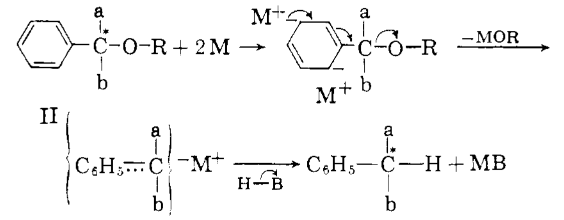
RECEIVED JANUARY 2, 1959

Cleavage of 2-benzyloxy-2-phenylbutane with potassium N-methylanilide in N-methylaniline gave 2-phenylbutane. This electrophilic substitution reaction is demonstrated to have occurred with predominating retention, and with a minimum of 26% stereospecificity. The steric course of cleavage of optically active 2-phenyl-2-butanol and 2-methoxy-2-phenylbutane with the alkali metals in various solvents to give 2-phenylbutane has been examined. With hydroxylic solvents and potassium metal, both the ether and alcohol gave hydrocarbon by reactions which were 14 to 31% stereospecific and which occurred with predominating inversion of configuration. From 8 to 10% stereospecificity with predominating retention of configuration was found when the alcohol was cleaved in the same solvents with lithium metal. Cleavage of the alcohol in benzene with potassium, or of the corresponding ether in diethyl ether with sodium–potassum alloy gave 2-phenylbutane by a reaction which occurred with 5–7% predominating retention of configuration. In these reactions, the 2-phenyl-2-butyl anion is considered to be an intermediate whose stereochemical fate is determined by the symmetry properties of its environment.

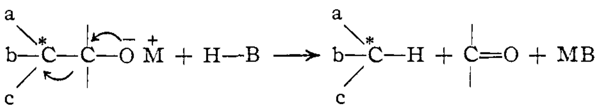
In past studies, the stereochemistry of electrophilic substitution at saturated carbon has been examined in systems whose initial reaction involved the breaking of carbon–carbon bonds.[2] The present paper reports systems in which carbon–oxygen bonds are broken and carbon–hydrogen bonds are made in the over-all reaction.

A survey of the literature revealed that two kinds of reactions might be used: (1) the base-catalyzed cleavage of benzyl ethers of general formula I[3]; (2) the metal–acid reductive cleavage of alcohols or ethers such as II.[4] In the systems studied in this paper, a, b, c, d and e were ethyl, methyl, phenyl, hydrogen and phenyl, respectively; R was either hydrogen or methyl, respectively.





Thus 2-phenylbutane was the product in all cases, which was also the product of cleavage of many systems of type III, which have been previously examined. This study allows a limited comparison to be made between systems which differ in the nature of their leaving groups and in the mode of formation

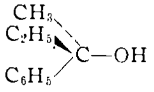


III

of the carbanion in the electrophilic substitution reaction at saturated carbon.

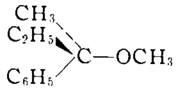
Results

The tertiary alcohol IV was resolved,[5] and converted to the benzyl and methyl ethers V and VI,[6] respectively. The configuration of IV relative to that of 2-phenylbutane (VII) has been established previously,[7] the configuration of the latter compound having been demonstrated.[8] The configurations and maximum rotations of these compounds are listed.



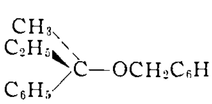
IV

$\alpha^{25}\text{D}$ +18.1°
(l 1 dm., neat)



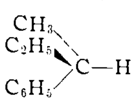
V

$\alpha^{25}\text{D}$ +41.6°
(l 1 dm., neat) (calcd.)



VI

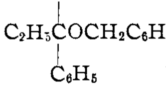
$\alpha^{25}\text{D}$ −24.0°
(l 1 dm., neat) (calcd.)



VII

$\alpha^{25}\text{D}$ +24.3°
(l 1 dm., neat)

Attempts were made to cleave ether VI in *t*-butyl alcohol with potassium *t*-butoxide at 195° (conditions under which 2-phenylbutane slowly racemizes),[2b] but no product (VII) could be isolated. Attempts were made to prepare compound VIII by treatment of *p*-methylsulfonylbenzyl chloride with



$C_2H_5\underset{C_6H_5}{\overset{CH_3}{C}}OCH_2C_6H_4SO_2CH_3$ VIII

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(1) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this 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); (e) D. J. Cram, F. Hauck, K. R. Kopecky and W. D. Nielsen, *ibid.*, **81**, 5767 (1959); (*f*) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *ibid.*, **81**, 5774 (1959).

(3) (a) D. Y. Curtin and S. Leskowitz, *ibid.*, **73**, 2630 (1951); (b) **73**, 2633 (1951); (c) C. R. Hauser and S. W. Kantor, *ibid.*, **73**, 1437 (1951). Previous references are quoted in these articles.

(4) A summary of references and general discussion has been given by A. J. Birch, *Quarterly Reviews*, **4**, 69 (1950).

(5) (a) H. H. Zeiss, THIS JOURNAL, **73**, 2391 (1953); (b) A. Davies, J. Kenyon and L. Salome, *J. Chem. Soc.*, 3148 (1957).

(6) H. H. Zeiss, THIS JOURNAL, **75**, 3154 (1953).

(7) D. J. Cram and J. Allinger, *ibid.*, **76**, 4516 (1954), and ref. 2c.

(8) D. J. Cram, *ibid.*, **74**, 2150 (1952).

TABLE I

RESULTS OF CLEAVAGES OF 2-PHENYL-2-BUTANOL (IV) AND OF 2-METHOXY-2-PHENYLBUTANE (V) WITH METALS AND ALCOHOLS

	Starting material							2-Phenylbutane[a]				
Run	Nature	Concn., *M*	α^{24-26}D[b]	Solvent	Metal	Final base concn., *M*	Temp., °C.	Yld., %	n^{25}D	α^{22-29}D[b]	% optical yield[c]	Predom. steric result
1	IV[d]	0.10	− 9.72°	$(CH_3)_3COH$	K	0.5	70	35	1.4879	+2.78°	21	Inv.
2	IV	.10	− 9.72	$(CH_3)_3COH$	K	1.5	70	35	1.4878	+2.10	15	Inv.
3	IV	.10	−14.2	$(CH_3)_2CHOH$	K	1.0	60	48	1.4875	+4.12	22	Inv.
4	IV	.10	+13.7	$CH_3(CH_2)_3OH$	K	2.0	65	10	1.4875	−3.52	19	Inv.
5	IV	.10	+13.7	C_2H_5OH	K	2.0	50	45	1.4866	−3.40	18	Inv.
6	IV	.10	−14.2	$C_6H_5NHCH_3$	K	0.5	100	30	1.4875	−0.04	0	Rac.
7[e]	IV	.36	+15.6	C_6H_6	K	0.36	72	10	1.4877	+1.14	6	Ret.
8	IV	.10	−14.2	$(CH_3)_3COH$	Li	2.0	60	4	1.4876	−0.60	9	Ret.
9	IV	.10	+13.7	$CH_3(CH_2)_3OH$	Li	2.0	60	3	1.4879	+0.40	9	Ret.
10	V[f]	.11	+37.1	$(CH_3)_3COH$	K	0.5	30	36	1.4872	−6.72	31	Inv.
11	V	.11	+37.1	$CH_3(CH_2)_3OH$	K	2.0	45	33	1.4872	−2.91	14	Inv.
12	V	.11	+37.1	$C_6H_5NHCH_3$	K	0.5	90	33	1.4875	+0.06	0	Rac.
13	V	.11	+37.1	$NH_3–CH_3OH$	Na	0.5	−33	69	1.4876	−0.04	0	Rac.
14	V	.46	+29.9	$(C_2H_5)_2O$	Na–K	..	25	31	1.4879	+1.15	7	Ret.

[a] Optically pure 2-phenylbutane has α^{25}D ±24.3° (*l* 1 dm., neat) and n^{25}D 1.4878 (ref. 8). [b] *l* 1 dm., neat. [c] Optical purity of 2-phenylbutane that would have been obtained had optically pure starting material been used. [d] Optically pure 2-phenyl-2-butanol has α^{22}D ±18.1° (*l* 1 dm., neat); ref. 5b. [e] Starting material, 62%, was recovered n^{25}D 1.5162, α^{25}D +15.8 (*l* 1 dm., neat). [f] Optically pure 2-methoxy-2-phenylbutane has αD ±41.6° (*l* 1 dm., neat) (calcd. value).

the potassium salt of 2-phenyl-2-butanol. Only *p,p'*-bis-methylsulfonio-*trans*-stilbene was obtained.

System VI was found to cleave in N-methylaniline–potassium N-methylanilide at 180° to give 2-phenylbutane. The reaction occurred *with predominating retention of configuration with an optical yield of 29%*. Part of the product was swept from the reaction mixture with nitrogen, whereas some remained behind. The fact that the latter product was of lower rotation than the former indicates that VII racemized somewhat under the conditions of its formation, and that the above optical yield was only a minimum value.

In Table I are recorded the results of reductive cleavages of optically active alcohol IV and ether V with alkali metals under a variety of conditions. In runs 1–5, IV was cleaved in a series of alcohols with potassium metal to give 2-phenylbutane (VII) with *predominating inversion of configuration* in optical yields ranging from 15 to 22%. In runs 10 and 11, V was cleaved with potassium metal in *t*-butyl alcohol and 1-butanol; VII was obtained in 31 and 14% optical yields respectively, and *the reductive cleavages occurred with predominating inversion of configuration*. In runs 6 and 12, IV and V were cleaved with potassium metal in N-methylaniline, and in run 13, V was cleaved in liquid ammonia–methanol. In all three reactions, racemic VII was obtained. Cleavage of alcohol IV in benzene with potassium metal (run 7) gave VII in about 6% optical yield *with predominating retention of configuration*. A similar result (run 14) was obtained when ether V was cleaved in diethyl ether with sodium–potassium alloy. In this run, traces of water present in the reaction mixture must have served as a source of protons. Low yields of VII were isolated when alcohol IV was cleaved with lithium metal in *t*-butyl alcohol (run 8) and 1-butanol (run 9). The reactions were both 9% stereospecific, and occurred with *predominant retention of configuration*. Similar treatment of ether V produced so little VII that the substance could not be isolated.

Attempts to convert 2-phenyl-2-butylamine to 2-phenylbutane by similar reductive cleavages failed.

Discussion

Base-catalyzed Cleavage of Benzyl Ether VII.—The base-catalyzed cleavage of the benzyl ether VII in N-methylaniline gave results which resemble those obtained when systems such as III were cleaved in the same solvent to give 2-phenylbutane as product.[2a] With either type of leaving group, electrophilic substitution occurred with predominating retention of configuration, accompanied by racemization. This cleavage reaction was accompanied by the ordinary base-catalyzed elimination reaction to give 2-phenylbutenes. Any bimolecular substitution reaction would have led to amine which would have been lost in the isolation procedures.

The similarity in stereochemical results suggests that the mechanism of the over-all reactions of systems such as I and III are similar to one another. However, the possibility exists that the potassium derivative (XI) of the benzyl ether undergoes a Wittig rearrangement[9] to give alkoxide IX which in turn cleaves to give 2-phenylbutane. In connection with this possibility, it is interesting to compare the results of the cleavage of IX[2a] and of XI. The two reactions were carried out at somewhat different temperatures, base strengths and reaction times, so a definitive answer as to whether they involved common intermediates cannot be given.[10]

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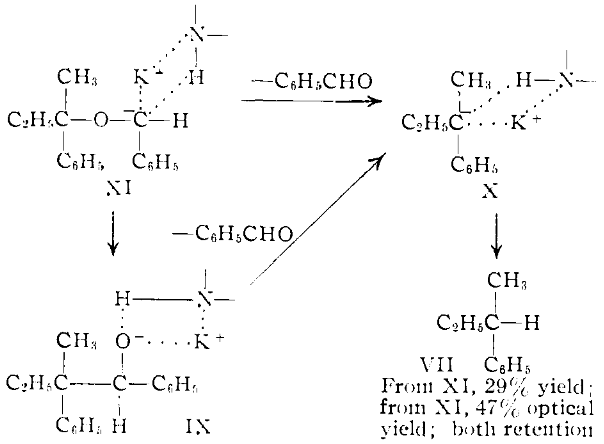
[9] (a) G. Wittig and L. Lohman, *Ann.*, **550**, 260 (1942); (b) G. Wittig and W. Happe, *ibid.*, **557**, 205 (1947); (c) G. Wittig and R. Clausnizer, *ibid.*, **588**, 145 (1954); (d) G. Wittig and E. Stahnecker, *ibid.*, **605**, 69 (1957).

[10] Any attempt to carry out these two reactions under identical conditions involves serious problems, particularly with respect to reaction times and base strengths. Since the reactions occur at different rates and the product must be swept out before it racemizes, either different temperatures or different reaction and *contact times* must be used. Since XI is undoubtedly a much weaker base than XI, more drastic reaction conditions are needed to make the latter base, and these conditions are more likely to racemize VII after it is formed. Another difficulty is that the base strength undoubtedly changes as

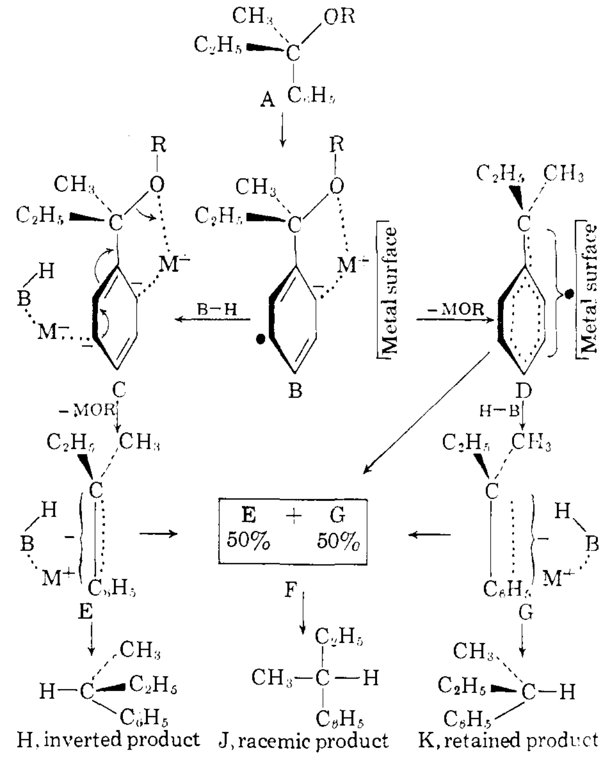


From XI, 29% yield; from XI, 47% optical yield; both retention

However, the fact that both reactions give product with predominant retention of configuration, and with a stereospecificity of about the same order of magnitude, supports the hypothesis that the two reactions involve common intermediates. These could be either IX and X, or just X. Thus XI could rearrange to IX by a mechanism involving only one transition state, and IX could then go to VII through X as an intermediate, which partitions between racemic product and that of retained configuration. A much more probable mechanism is that XI decomposes to give X which in turn gives VII. An intermediate such as X (minus the mole of solvent) is probably also involved in the Wittig rearrangement, which is ordinarily carried out in non-proton donating solvents. The possibility that intermediates intervene in this rearrangement has been discussed previously.[3a,3c,9c,9d]

Metal–Solvent Reduction of 2-Phenyl-2-butanol (IV) and of 2-Methoxy-2-phenylbutane (V).—The data of Table I coupled with other results[2] clearly indicate that different intermediates are involved in the reductive cleavage of II than in the base-catalyzed cleavage of either compounds of type I or III. The stereochemical direction of the electrophilic substitution reaction which accompanies the cleavage of either II or III can be directed toward predominant retention, inversion or racemization by variation of solvent or cation involved. However, the two types of systems react quite differently to particular solvents and particular metals. Thus systems such as II cleave with predominating inversion in *t*-butyl alcohol with potassium, but with predominating retention in the same solvents with lithium. Systems III cleave only with predominating retention in this solvent and with either potassium or lithium alkoxide as base. Systems II cleave in N-methylaniline to give totally racemic product, whereas III gives product of largely retained configuration in this solvent. Although both types of systems give predominating retention in non-proton-donating solvents such as benzene or ethers, the reactions of III are highly stereospecific whereas those of II are not. In spite of these marked differences in steric course, it is highly probable that both reactions involve carbanion intermediates, whose stereochemical fates differ because of differences in the shapes of their solvent envelopes. The mechanism of electrophilic substitution in systems such as III have been discussed in detail previously.[2f] A discussion of mechanism of substitution of II centers around the formulas of Chart I.

CHART I



Convincing evidence has been gathered[4] that the reductive fission of allyl or benzyl alcohols or ethers occurs by a multi-stage mechanism, the first step of which is the addition of one or two metal atoms to the unsaturated system. As applied to the systems at hand, this stage can be represented as A → B, in which a metal atom is removed from a metal surface. It is reasonable to suppose that the metal cation becomes coördinated with the electrons of the hydroxyl or methoxyl group of B. This intimate ion-pair might partition between C and D. In passing to C, B could either accept M^+ from the medium and an electron from the metal surface, or B could turn over and accept a second metal atom from the metal surface to give the bis-ion pair, C. With either alternative, the metal cations are on the opposite sides of the plane of the benzene ring in C, and are roughly at opposite ends, so that like charges can be as far from one another as possible. In C, one metal cation is coördinated with the benzyl–oxygen, and the other with a proton-donating solvent molecule. This dianion stabilizes itself by loss of MOR to give the intimate ion-pair E. This species either collapses to give product of inverted configuration (H), or if it lasts long enough, goes to F (an equal-molar mixture of E and G) which goes to racemic product (J). In an alternate route, B stabilizes itself by loss of MOR to give radical D. This radical reacts with the metal surface to give

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the reaction proceeds since benzaldehyde is converted into some sort of conjugate base which is weaker than XI, but possibly comparable to IX.

either asymmetric ion-pair G, or if it lasts long enough to lose its original orientation with respect to the metal surface, then F is produced. Intimate ion-pair G either collapses to give product of retained configuration (K), or goes to F by cationic exchange and thence to racemic material (J).

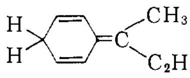
This mechanistic scheme provides a reasonable explanation for the results of Table I. The 14–31% net inversion observed in runs 1–5, 10 and 11 is attributed to a dominance of mechanism A → B → C → E → H over A → B → D → G → K. Certain trends are apparent in these data. The results suggest that higher stereospecificity is associated with lower temperatures, with tertiary or secondary alcohols (as compared with primary) as solvent, and with lower final concentration of metal alkoxides. All three of these trends should favor process E → H over E → F → J. The conversion of E → F involves metal cations, and should be accelerated by an increase in metal cation concentration at the expense of E → H. Since E → F is polymolecular and E → H monomolecular, the latter should be favored by lower temperatures. Since tertiary and secondary alcohols are more basic than primary, the former should be more tightly bound in E and proton capture (E → H) should be favored accordingly. However, steric effects would operate in the opposite direction.

In runs 6, 12 and 13, only racemic material was obtained. In these experiments either an amine or ammonia was employed as solvent. It is possible that IV and V reacted by way of A → B → D → F → J for the following reasons. Ammonia and amine solvents are known to dissolve the alkali metals and solvate their electrons, and possibly in these solvents, the metal surface is absent in B and D in these solvents. Since the asymmetry of D depends on its orientation with respect to a metal surface, the stereospecific process A → B → D → G → K disappears and is replaced by A → B → D → F → J, which gives racemic product. The step B → C might be faster in the presence of a metal surface than in a homogeneous system because in the former case the reactants are already near to one another. Thus process B → D might be favored in ammonia or amine solvents over B → C with the result that only racemic material is produced.

In runs 7–9 and 14, 2-phenylbutane is produced in optical yields of 5.5 to 9% with predominating retention of configuration. This result is attributed to a predominance of mechanism A → B → D → G → K over A → B → C → E → H, and to an over-all predominance of A → B → D → F → J over both of the stereospecific processes. In runs 8 and 9, lithium was employed, and the 2-phenylbutane produced was of predominantly retained configuration, whereas in runs 2 and 5, potassium was used with the same respective solvents, and the product was of predominantly inverted configuration. This result correlates with the much higher activity of a molten potassium as compared with a solid lithium surface with respect to reaction stage A → B. A similar difference can be expected for B → C, but not for the competing process B → D. Although an inactive surface such as lithium should favor F in the partitioning of D between F and G, a small residual amount of product could arise by D → G → K.

In runs 7 and 14, the reactions were conducted in non-proton-donating solvents, and the concentrations of B–H were very low. The low predominance of retention observed can be correlated with the low concentration of B–H in the medium. Stage B → C involves a mole of B–H whereas B → D does not, and therefore the rate of the former transformation should be depressed by low concentrations of B–H. Thus A → B → D → G → K should dominate over A → B → C → E → H. Lower stereospecificity is observed in the reaction since to some extent the solvent (ether or benzene) is probably able to replace B–H in C, G and E, and as a result these species tend to go to F, which can only give racemic product.

It is conceivable that small amounts of racemic 2-phenylbutane (VII) was produced in these reactions by collapse of species such as E or G to give trienes similar to XII, which subsequently rearrange to VII. In this connection, Russell[11] has observed that small amounts of nuclearly-deuterated isopropylbenzene are produced when 2-phenyl-2-propylpotassium is decomposed with various deuterio-acids.



XII

Experimental

(−)-2-Benzyloxy-2-phenylbutane (VI).—To 2.12 g. (0.0544 mole) of clean potassium in 150 ml. of dry benzene was added 8.2 g. (0.0547 mole) of 2-phenyl-2-butanol (IV), $\alpha^{25}\text{D}$ +15.6° (*l* 1 dm., neat), 86% optically pure.[5b] The mixture was stirred at reflux temperature until all the metal had reacted. To the solution was added 15.0 g. (0.088 mole) of benzyl bromide, and the mixture was allowed to reflux for 2 hours, at the end of which time a white precipitate had separated. The reaction mixture was allowed to stand at 25° for 10 hours, and shaken with 100 ml. of water. The aqueous layer was washed with pure pentane, and the combined organic layers were washed with water, dried and evaporated through a fractionating column. The residual oil was chromatographed on 500 g. of activated alumina. Elution of the hydrocarbon fraction with 500 ml. of pure pentane gave 0.754 g. of 2-phenylbutane (10% yield), $n^{25}\text{D}$ 1.4877, $\alpha^{25}\text{D}$ +1.14° (neat, *l* 1 dm.), 5.4% optical yield. This product was produced by reductive fission of 2-phenyl-2-butanol by the potassium metal as a reaction which competed with the formation of the potassium alkoxide. The alcohol itself provided the protons needed for reaction. This result is labeled as *run 7* in Table I.

The ether product mixed with benzyl bromide was eluted from the chromatograph column with 1400 ml. of pure pentane. This material was freed of benzyl bromide as follows. The mixture was heated at 100° with 6 *N* sodium hydroxide solution for 10 hours, and the resulting solution was extracted with pure pentane. The pentane extract was dried, evaporated, and the residue was chromatographed on 60 g. of activated alumina. The desired benzyl ether was eluted with pentane and distilled at 1 mm. pressure to give 5.60 g. (43% yield) of VI, $n^{25}\text{D}$ 1.5481, $\alpha^{25}\text{D}$ −20.7° (*l* 1 dm., neat). A small sample of this material was redistilled for analysis.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.95; H, 8.26.

Cleavage of (−)-2-Benzyloxy-2-phenylbutane (VI) in N-Methylaniline.—Potassium metal (0.32 g. or 0.0082 mole) was dissolved in dry N-methylaniline (14 ml.) under an atmosphere of dry nitrogen, and 2.00 g. (0.00833 mole) of VI, $\alpha^{25}\text{D}$ −20.7° (neat, *l* 1 dm.), was added at room tem-

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(11) G. A. Russell, This Journal, **81**, 2017 (1959).

perature. The resulting dark brown mixture was heated in a bath at 180°, and stirred in a stream of dry nitrogen to aid in the distillation of 2-phenylbutane. The receiver was cooled to −78° to trap the product. After 1.5 hours, 1 ml. of distillate had been collected, and the reaction was interrupted. The distillate was shaken with a mixture of 20 ml. of pure pentane and 5 ml. of 4 *N* hydrochloric acid. The organic layer was washed with successive portions of the acid solution, and then with water. The organic layer was dried, evaporated, and the residue was chromatographed on 60 g. of alumina. The product was eluted with 500 ml. of pure pentane, which was evaporated to an oil through a Vigreux column. The residue was treated with 2,4-dinitrobenzenesulfenylchloride in acetic acid to remove olefin by the method reported previously,[2a] and the 2-phenylbutane was recovered and distilled to give 0.226 g. (20% yield) of material, $n^{25}\mathrm{D}$ 1.4878, $\alpha^{27}\mathrm{D}$ +5.42° (neat, *l* 1 dm.) (29% stereospecificity).

The residue in the reaction pot was subject to the same procedure to give 0.383 g. (34% yield) of additional 2-phenylbutane, $n^{25}\mathrm{D}$ 1.4878, $\alpha^{27}\mathrm{D}$ +4.27 (neat, *l* 1 dm.) (20% stereospecificity). An odor of benzaldehyde was noted for a yellow liquid which was obtained from latter fractions of the chromatograph column.

Attempt to Prepare *p*-Methylsulfoniobenzyloxy-2-phenylbutane.—An attempt was made to prepare this substance by the reaction of the potassium alkoxide of 2-phenyl-2-butanol with *p*-methylsulfoniobenzyl chloride. The latter compound was prepared as follows.

The substance, *p*-methylsulfoniobenzoic acid,[12] was converted to its ethyl ester in 92% yield by the usual procedure with ethanol and concentrated sulfuric acid. The substance had m.p. 95–96°. This material (25.5 g., 0.112 mole) was added by soxhlet extraction (2 hours) to a suspension of 5.0 g. (0.132 mole) of lithium aluminum hydride in 250 ml. of dry ether. The resulting mixture was refluxed for 6 hours, and cautiously mixed with water. The resulting solution was evaporated to dryness, and the resulting solid was extracted in a soxhlet with ether for 10 hours. The ether mixture was evaporated to dryness, and the residue was recrystallized from ethanol–benzene to give 19.9 g. (95% yield) of colorless flakes of *p*-methylsulfoniobenzyl alcohol, m.p. 84.5–85.0°.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.59; H, 5.41. Found: C, 51.78; H, 5.64.

This material was converted to its chloride derivative as follows. Thionyl chloride (15 ml.) and *p*-methylsulfoniobenzyl alcohol (4.5 g.) were mixed and, after the vigorous reaction had subsided, the reaction mixture was held at reflux for 0.5 hour. The excess thionyl chloride was then evaporated at 30 mm. pressure, and the residual oil was distilled at 180° (bath temperature) and 0.8 mm. pressure to give a colorless liquid which crystallized when allowed to stand. Recrystallization of this material from benzene gave colorless needles, 4.75 g. (96% yield) of *p*-methylsulfoniobenzyl chloride, m.p. 78.5–79°.

Potassium metal (0.52 g. or 0.0133 mole) was added to a solution of racemic 2-phenyl-2-butanol (2.00 g. or 0.0133 mole) in 50 ml. of benzene. After reaction, the resulting solution was cooled to 0° and 2.73 g. (0.0133 mole) of *p*-methylsulfoniobenzyl chloride was added with stirring. The dark green solution was stirred at 0° for 2 hours, during which time a solid separated. The mixture was treated with 50 ml. of water, and the resulting mixture of liquids and solid was filtered. The filtrate was recrystallized from acetone to give 1.04 g. of colorless leaflets, m.p. 305–306.5°. This material possessed an ultraviolet absorption spectrum in chloroform which possessed $\lambda_{\max}$ at 317 mμ (log ε 4.38) and a shoulder at 332–338 mμ, and which resembled that of *trans*-stilbene.[13] The substance is probably *p,p'*-bis-methylsulfonio-*trans*-stilbene, and gave an analysis for this compound.

Anal. Calcd. for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.80. Found: C, 57.09; H, 4.94.

From the filtrates was isolated 0.217 g. of 2-phenylbutane, $n^{25}\mathrm{D}$ 1.4881, and 1.564 g. of 2-phenyl-2-butanol, $n^{25}\mathrm{D}$ 1.5161.

Preparation of 2-Phenyl-2-butylamine and Derivatives.—A mixture of 2-methyl-2-phenylbutanoyl chloride[2a] (15.0 g. or 0.76 mole) in 80 ml. of dry xylene and activated sodium azide[14] (5.5 g., or 0.084 mole) was heated at 85° for 3 hours and then at 115° for 1.5 hours. After 4 hours, 1690 ml. of nitrogen had been collected. The mixture was cooled, and the solid was collected and washed with hot benzene. The filtrate was mixed with 20 ml. of concentrated hydrochloric acid, and heated at 100° for one hour. The solvents were evaporated and the resulting solid was recrystallized from methanol–ether to give 13.5 g. (95% yield) of the amine hydrochloride, m.p. 242°.

Anal. Calcd. for $C_{10}H_{16}NCl$: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.35; H, 7.51; N, 5.36.

A sample of the above amine was converted to its N-benzenesulfonate in 53% yield by the usual method, m.p., 126–127°.

Anal. Calcd. for $C_{16}H_{19}O_2SN$: C, 66.61; H, 6.62. Found: C, 66.61; H, 6.69.

(+)-2-Methoxy-2-phenylbutane (V).—From 7.12 g. of (+)-2-phenyl-2-butanol, $n^{25}\mathrm{D}$ +16.1° (*l* 1 dm., neat), was obtained 7.73 g. of V, $\alpha^{30}\mathrm{D}$ +37.1° (*l* 1 dm., neat.)

Cleavage of (+)-2-Methoxy-2-phenylbutane with Sodium Potassium Alloy (Run 14).—To a solution of 10 ml. of dry ether and 0.76 g. of (+)-2-methoxy-2-phenylbutane, $\alpha^{25}\mathrm{D}$ +29.9° (neat, *l* 1 dm.), was added 0.58 g. of sodium–potassium alloy in a dry nitrogen atmosphere. The resulting mixture was stirred at room temperature under nitrogen for 24 hours, and then dry carbon dioxide gas was passed into the dark red mixture until the color changed to light brown. The resulting mixture was shaken with water, and the ether phase was dried, evaporated, and the residual oil was distilled to give 0.94 g. (31% yield) of 2-phenylbutane, $n^{25}\mathrm{D}$ 1.4879, $\alpha^{23}\mathrm{D}$ +1.15° (neat, *l* 1 dm.). The infrared spectrum of this material was identical to that of an authentic sample.

The aqueous layer was acidified, and extracted with ether. The ether layer was washed with water, dried, evaporated, and the residue was distilled to give 0.14 g. (17% yield) of impure 2-methyl-2-phenylbutanoic acid, $\alpha^{23}\mathrm{D}$ +0.26 (*c* 48.1 in benzene, *l* 1 dm.). When recrystallized from pentane, colorless needles of the acid were obtained, $\alpha^{31}\mathrm{D}$ 0.00° (*c* 69 in benzene, *l* 1 dm).

Reductive Cleavage of (+)-2-Methoxy-2-phenylbutane (V) with Sodium in Liquid Ammonia–Methanol (Run 13).—A solution of 20 ml. of dry methanol, 100 ml. of dry ammonia and 1.00 g. (0.0061 mole) of V, $\alpha^{30}\mathrm{D}$ +37.1° (neat, *l* 1 dm.), was prepared, and to this solution was added 1.405 g. (0.609 mole) of sodium metal in small pieces over a period of one hour. Ether (100 ml.) was added to the mixture, and the ammonia was allowed to evaporate. The resulting solution was evaporated through a Vigreux column, and the residual oil was adsorbed on 200 g. of activated basic alumina (ignited 20 minutes at 600°). The 2-phenylbutane product was eluted with the first 400 ml. of pure pentane, and was isolated in the usual way to give 0.305 g., $n^{25}\mathrm{D}$ 1.4876, $\alpha^{28}\mathrm{D}$ −0.04° (neat, *l* 1 dm.).

Reductive Cleavage of (−)-2-Phenyl-2-butanol (IV) in *t*-Butyl alcohol with Lithium (Run 8).—To a dry flask in a nitrogen atmosphere was added 1.00 g. (0.00667 mole) of IV, $\alpha^{23}\mathrm{D}$ −14.2° (neat, *l* 1 dm.), dissolved in 67 ml. of dry *t*-butyl alcohol. To this stirred solution held at 60° was added in very small pieces 0.925 g. (0.133 gram atom) of lithium metal. After reaction was complete, the reaction mixture was cooled, treated with 20 ml. of methanol, and then shaken with a mixture of 150 ml. of pure pentane and 150 ml. of water. The aqueous phase was extracted with pure pentane, and the combined organic layers were washed successively with six 100-ml. portions of water. The organic phase was dried, evaporated through a small fractionating column, and the residue was chromatographed on 60 g. of activity I neutral alumina. The hydrocarbon fraction was washed from the column with 400 ml. of pure pentane, the solvent was evaporated through a fractionating column, and the residue was distilled at 40 mm. pressure to give 0.116 g. of crude 2-phenylbutane contaminated with 2-phenylbutenes. Olefin was removed from the mixture with 2,4-dinitrobenzenesulfonyl chloride by a procedure described previously.[2a] The hydrocarbon product amounted to 0.037 g. of 2-phenylbutane, $n^{25}\mathrm{D}$ 1.4876, $\alpha^{22}\mathrm{D}$ −0.60 (neat, *l* 1 dm.).

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[12] A. T. Fuller, I. M. Tonkin and J. Walker, *J. Chem. Soc.*, 633 (1945).

[13] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 126.

[14] P. A. S. Smith, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 382.

This rotation was taken of a mixture that consisted of 0.037 g. of the product diluted with racemic 2-phenylbutane to 0.101 g.

Reductive Cleavage of (−)-2-Phenyl-2-butanol (IV) in *t*-Butyl alcohol with Potassium Metal (Run 1).—A solution of 1.00 g. (0.00667 mole) of alcohol IV, $\alpha^{26}D$ −9.72° (neat, *l* 1 dm.), in 67 ml. of dry *t*-butyl alcohol under dry nitrogen was heated to 70° and stirred. To this solution over a period of 45 minutes was added in small pieces 1.305 g. (0.0033 mole) of clean potassium metal.

The reaction mixture was cooled and shaken with a mixture of 200 ml. of ether and 200 ml. of water. The aqueous layer was extracted with 100 ml. of pure pentane, and the combined organic layers were washed with water. The 2-phenylbutane product was isolated as in run 8, except that no olefin was present. The 2-phenylbutane product amounted to 0.317 g. (35% yield), $n^{25}D$ 1.4879, $\alpha^{24}D$ +2.78° (*l* 1 dm., neat) (21% stereospecificity).

Reductive Cleavage of (+)-2-Methoxy-2-phenylbutane (V) in N-Methylaniline with Potassium (Run 12).—A solution of 1.00 g. (0.00609 mole), $\alpha^{24}D$ +37.1° (neat, *l* 1 dm.), of ether V in 61 ml. of pure N-methylaniline was heated to 90° under nitrogen and stirred. To this solution was added 1.190 g. (0.0305 gram atom) of potassium metal. The mixture was stirred vigorously, and it turned black very quickly although the potassium reacted slowly. After 8 hours, the mixture was cooled, and the excess potassium was decomposed with methanol. The reaction mixture was shaken with a mixture of 200 ml. of pure pentane–200 ml. of water. The organic layer was extracted with four 100-ml. portions of 6 *N* sulfuric acid, washed with water, dried and evaporated through a fractionating column. The residue was chromatographed, and the 2-phenylbutane product isolated as in the other runs (no olefin was present) to give 0.270 g. (28% yield) of material, $n^{25}D$ 1.4878, $\alpha^{26}D$ +0.06° (neat, *l* 1 dm.).

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. VIII. Diarylolefin–Diarylalkyl Cation Equilibria[1]

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RECEIVED APRIL 8, 1959

The equilibria between diarylalkyl cations and their corresponding olefins and alcohols were studied as a function of sulfuric acid concentration. It was found that the protonation of diarylolefins, although an equilibrium of the $BH^+ = B + H^+$ type, widely deviates from the well-known eq., $H_0 = pK_{BH^+} + \log (c_B/c_{BH^+})$. The manner of the deviation can be quantitatively predicted from a consideration of activity coefficient data. The diarylolefins are usually, but not always, stable in respect to their corresponding alcohols in sulfuric acid concentrations where half of the olefin is converted into the diarylalkyl cation. Deuterium experiments showed that *t*-alkyl cations are present in small amounts in equilibrium with diarylalkyl cations. The hexamethylbenzene-protonated hexamethylbenzene equilibrium was examined. The spectra and structure–stability relationships of arylmethyl cations were re-examined with the aid of simple LCAO MO theory.

Diarylolefin–Diarylalkyl Cation Equilibria.—In earlier papers in this series, it was established that in aqueous mineral acids, arylmethanols were in equilibrium with their corresponding arylmethyl cations and that the equilibria shifted with acidity according to eq. 1.[2,3]

$$H_R = pK_{R^+} + \log (c_{ROH}/c_{R^+}) \qquad (1)$$

These equilibria studies led to the evaluation of the H_R acidity function[4] in aqueous sulfuric acid,[2] perchloric acid[3] and nitric acid.[3] In all of this previous work, arylolefins were eliminated from consideration by choosing arylmethanols which were structurally prevented from directly dehydrating to olefins. It now seemed appropriate to extend these studies to arylolefins. The present study was restricted to 1,1-diarylolefins.

The addition of sulfuric acid solutions of 1,1-diphenylethyl, 1,1-diphenylpropyl, 1,1-diphenyl-2-methylpropyl, 1,1-bis-(4′-methylphenyl)-ethyl, 1,1-bis-(4′-methoxyphenyl)-ethyl and 1,1-bis-(4′-chlorophenyl)-ethyl cations to water led to the recovery of olefin and/or olefin dimer (*cf.* Experimental). It was thus concluded that in general the diarylolefins were stable in respect to the diarylalkanols in sulfuric acid solutions. This result permitted the treatment of diarylolefin–diarylalkyl cation equilibria to be simplified by neglecting the diarylalkanol concentration.

A complete exception to the above generalization was the 9-isopropylxanthyl cation. This cation quantitatively gave 9-isopropyl-9-xanthenol on addition of water to a solution of the cation in 25% sulfuric acid.

The equilibria between arylolefins (ol) and arylmethyl cations (R^+) can be predicted to follow eq. 4 on the basis of the following derivation. The definition of the H_R acidity function is eq. 2,[2] and the *pK* expression for arylolefin–arylmethyl cation equilibria is eq. 3. Previous work on activity coefficient behavior in sulfuric acid solutions[5] would indicate that $f_{ROH} = f_{ol}$. Also, since $f_R{}^+$ was the same for $R = Ar_3C^+$ or Ar_2CH^+, it is reasonable to assume that f_{R^+} is the same for Ar_2CH^+ and $Ar_2C(alkyl)^+$. Combining these relations with eqs. 2 and 3 gives eq. 4. The significance of the prime on $pK_R{}'_+$ is to distinguish this pK for arylolefin–arylmethyl cation equilibria from pK_{R^+} which had been used for the arylmethanol–arylmethyl cation equilibria.

$$H_R = -\log (a_{H^+}) + \log (a_{H_2O}) + \log (f_{R^+}/f_{ROH}) \qquad (2)$$

$$pK'_{R^+} = -\log (a_{H^+}) + \log (c_R/c_{ol}) + \log (f_{R^+}/f_{ol}) \qquad (3)$$

$$H_R - \log (a_{H_2O}) = pK'_{R^+} + \log (c_{ol}/c_{R^+}) \qquad (4)$$

Data on the diarylolefin–diarylalkyl cation equilibria are summarized in Table I. As predicted, the data satisfactorily fit eq. 4. It might have been thought that since these equilibria are of the $BH^+ = B + H^+$ type, the data would have

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(1) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. This research was also supported in part by a grant from the National Science Foundation. Grateful acknowledgment is hereby made of this support.

(2) N. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

(3) N. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

(4) The decision to use the symbol H_R rather than C_0 and J_0, which were previously employed, is explained in ref. 3.

(5) N. Deno and C. Perizzolo, THIS JOURNAL, **79**, 1345 (1957).