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Neighboring Carbon and Hydrogen. IX. Neighboring Phenyl in Benzylmethylcarbinyl *p*-Toluenesulfonate[1,2]

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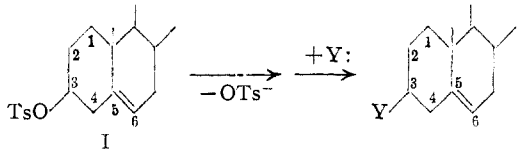
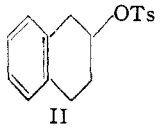
The group of neighboring electronic systems which effect over-all retention of configuration in nucleophilic replacement includes the π-electron-containing neighboring olefinic linkage as in the *i*-sterol or homoallylic phenomenon. The phenyl group in benzylmethylcarbinyl *p*-toluenesulfonate may serve as the π-electron center, phenyl group participation competing well enough with solvent participation so that formolysis proceeds with predominating retention of configuration. Ethanolysis, acetolysis and formolysis rates for benzylmethylcarbinyl *p*-toluenesulfonate (and *p*-bromobenzenesulfonate) and also the *p*-methoxybenzylmethylcarbinyl and 3-*p*-anisyl-2-butyl esters together with previously determined solvolysis rates for the isopropyl and 3-phenyl-2-butyl esters are instructive. The rates are in line with: (a) an increasing importance of phenyl group participation relative to solvent participation in the solvent sequence, EtOH < AcOH < HCOOH, for benzylmethylcarbinyl *p*-toluenesulfonate; (b) a substantial rate enhancement by the *p*-methoxyl group and also the β-methyl group under conditions (*e.g.*, formic acid as a solvent) where phenyl group participation is well-developed. A possible correlation between effects in the ultraviolet spectrum of the corresponding ketones and effects on rates or stereochemical results of solvolysis of related *p*-toluenesulfonates is pointed out.

In the *i*-sterol or homoallylic phenomenon, nucleophilic substitution at C_3 of a substance such as cholesteryl *p*-toluenesulfonate (I) proceeds with over-all retention[5,6,7] of configuration due to participation of the electron cloud of the neighboring olefinic system in the replacement process. Recog-



I

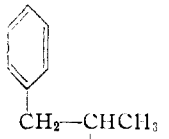
nition of this role of the π-electron center at C_5 in the replacement reactions at C_3 of the Δ^5-sterols enlarges the group of neighboring electronic systems (*e.g.*, neighboring CO_2^-, Br, OAc, etc.) which effect over-all retention of configuration in nucleophilic replacements.[8] In considering the scope of this kind of participation one is led to consider the possibility of similar control of stereochemistry by an aromatic group. Analogously, Stoll[9] was led to measure the ethanolysis rate of the *p*-toluenesulfonate of *ac*-tetrahydro-β-naphthol (II) in connection with the *i*-sterol phenomenon. It occurred independently to us and to Professor C. K. Ingold[10]



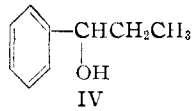
II

that the phenyl group, as in the classical[11] system, benzylmethylcarbinyl *p*-toluenesulfonate (III), might serve as the neighboring π-electron-containing group, and in this paper we report the results of an investigation of the solvolysis of this material and some related matters.

The ethanolysis of benzylmethylcarbinyl *p*-toluenesulfonate (III) was investigated early by Phillips,[11] the ethyl ether having a rotation *ca.* 85% of theoretical inversion being the predominant result. Phillips[11] also investigated the acetolysis of this toluenesulfonate and obtained an acetate with a largely inverted configuration, the final carbinol from saponification of the acetate having a rotation *ca.* 48% as large as the original. However, it was not clear[12] to us whether potassium acetate was used in the glacial acetic acid and to what extent the steric result was due to bimolecular displacement by acetate ion. Acetolysis by us of benzylmethylcarbinyl *p*-toluenesulfonate in 0.1 *M* solution in acetic acid without dissolved potassium acetate gave acetate and final saponified alcohol in *ca.* 60% yield, with predominant inversion and 29% survival of optical activity. Control experiments demonstrated that racemization of active benzylmethylcarbinyl acetate was not important under the reaction conditions. Thus it is clear that Phillips[11] had actually employed potassium acetate in his work, but that predominant inversion of configuration is still the steric result in glacial acetic acid alone.



III



IV

V

The results in ethanol and acetic acid follow the general order of solvents arranged for decreasing tendency for back-side intervention. This order can be quite well inferred from our previous discussion[13] of solvolysis and from available facts on the extent of predominant inversion in solvolysis of optically active derivatives[14] or the size of the gap

(1) Supported in part by the Office of Naval Research.

(2) (a) Some of the kinetic results of this paper were reported in summary before the Organic Division of the American Chemical Society, St. Louis, Mo., Sept., 1948. (b) Some of the remaining material was presented in summary at Montpellier, France, April 26, 1950 [*Bull. soc. chim.*, [5] **18**, C55 (1951)].

(3) Partly abstracted from M.S. Thesis of Mary (Anderson) Brown, U. C. L. A., January, 1950.

(4) National Institutes of Health Postdoctoral Fellow, 1947-1948.

(5) Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937).

(6) Shoppee, *J. Chem. Soc.*, 1147 (1946).

(7) Winstein and Adams, THIS JOURNAL, **70**, 838 (1948).

(8) *E.g.*, (a) Winstein, Hess and Buckles, *ibid.*, **64**, 2796 (1942); (b) Winstein, Paper at Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of Abstracts.

(9) Stoll, *Z. physiol. Chem.*, **246**, 1 (1937).

(10) Private communication, Spring, 1947.

(11) Phillips, *J. Chem. Soc.*, 44 (1923).

(12) Potassium acetate is mentioned in the title of the experiment but not in the text.

(13) Winstein, Grunwald and Jones, THIS JOURNAL, **73**, 2700 (1951).

(14) *E.g.*, Steigman and Hammett [*ibid.*, **59**, 2536 (1937)] and Hughes, Ingold and Scott [*J. Chem. Soc.*, 1201 (1937)] for C_6H_5CHCl-CH_3.

between the compositions of product from isomeric allylic halides.[15] From these kinds of considerations, one derives a solvent order something as follows: EtOH > MeOH > H_2O > AcOH > HCOOH. Therefore, formolysis of III was investigated and this indeed proceeded with predominant retention of configuration.

Formolysis of benzylmethylcarbinyl *p*-toluenesulfonate (III) gave rise to formate product, and subsequently carbinol on saponification, in yields up to 80%. The carbinol possessed physical properties in agreement with those of benzylmethylcarbinol, and it yielded the proper acid phthalate derivative. A more accurate indication of the extent of possible contamination of the material with isomeric carbinols could be obtained from the infrared spectrum in the 9.5–10.5 μ region. In this region, benzylmethylcarbinol does not absorb, while 1-phenyl-1-propanol (IV), the product of rearrangement involving migrating hydrogen (or product of addition to 1-phenylpropene), and 2-phenyl-1-propanol (V), the product of rearrangement involving migrating phenyl, each show two absorption bands. In Fig. 1 are given the infrared absorption spectra in the 9.5–10.5 μ region for the formolysis products, as well as for 1-phenyl-1-propanol (2-phenyl-1-propanol is essentially identical), and mixtures of benzylmethylcarbinol with 2.11, 4.29 and 7.68% 1-phenyl-1-propanol (IV). From these spectra it is clear that the proportion of contaminant is no more than 2.5 ± 0.5% in the product of formolysis at 75° and no more than 5.0 ± 0.5% in the product of formolysis at 50°. This degree of impurity is insufficient to affect greatly the interpretation of the results of solvolysis of optically active benzylmethylcarbinyl *p*-toluenesulfonate III.

The formolysis of optically active benzylmethylcarbinyl *p*-toluenesulfonate (III) in 0.1 *M* solution at 80° gave rise to a final alcohol with the same sign of rotation as that of the original starting alcohol, the survival of activity being *ca.* 30%. Much of the loss of activity must be ascribed to acid-catalyzed racemization of the product, however, for formolysis of III in 0.17 *M* solution, 0.20 *M* in sodium formate, gave 67% survival of activity.

In order to check on the extent to which the steric results were being affected in the direction of inversion by the formate ion and water present in the formic acid solvent, the formolysis was repeated in specially dried formic acid and at a formate ion concentration of 0.10 *M* instead of 0.20 *M*. Here the result was 70% survival of activity, this apparently being not far from the result which corresponds to formolysis in dry formic acid.

It seemed possible that the retention of configuration observed in formolysis was due to appearance of a reaction which depended on a reducing action of formic acid and sulfur–oxygen cleavage rather than alkyl–oxygen cleavage. However, this new type reaction in formic acid would produce toluenesulfinic acid rather than toluenesulfonic, and this possibility was eliminated by isolation of toluenesulfonic acid in high yield from formolysis of benzylmethylcarbinyl and also ethyl toluenesulfonate. The evidence then is that the solvolysis in formic acid which is attended by predominant retention of configuration is a conventional one.

(15) (a) Young, Winstein, Webb and Goering, unpublished work; (b) Young, Paper before 12th National Organic Symposium, Denver, Colorado, June 12, 1951, page 21 of Abstracts.

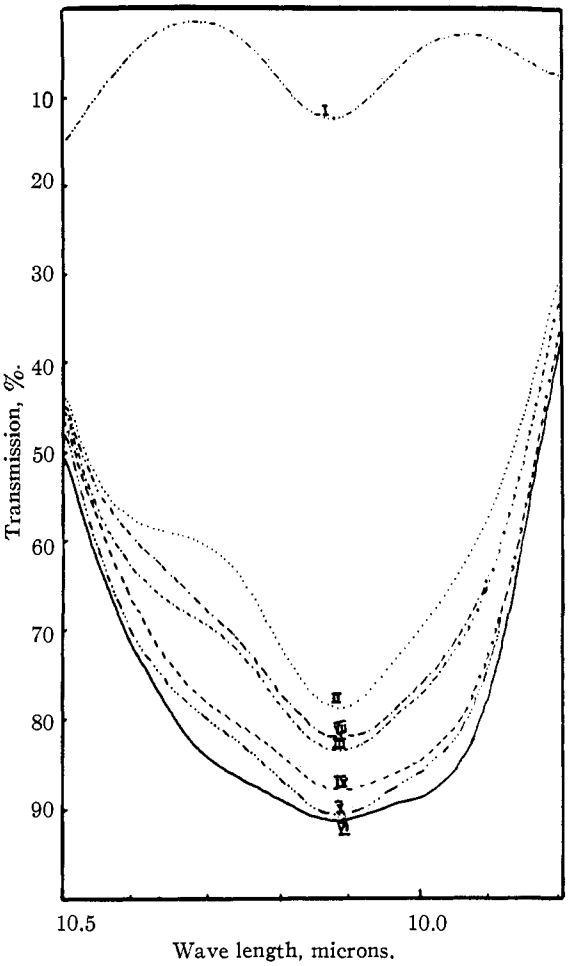


Fig. 1.—Infrared spectra of benzylmethylcarbinol and possible contaminant: I, pure 1-phenyl-1-propanol (1-P-1-P); II, mixture of benzylmethylcarbinol (BMC) and 7.68% 1-P-1-P; III, mixture of BMC and 4.29% 1-P-1-P; IV, 75° formolysis product; V, mixture of BMC and 2.11% 1-P-1-P; VI, pure BMC; VII, 50° formolysis product.

The steric results of ethanolysis, acetolysis and formolysis, summarized in one of the possible ways in Table I, are taken to indicate the increasing importance of phenyl group participation in the solvent sequence: EtOH < AcOH < HCOOH. In formic acid as a solvent, participation of phenyl competes sufficiently well with solvent participation to make retention of configuration the predominant over-all steric result. The simplest manner in which to discuss this competition is in

TABLE I

STERIC RESULTS OF SOLVOLYSIS OF BENZYLMETHYLCARBINYL *p*-TOLUENESULFONATE

Solvent	Inversion	Retention
EtOH	93	7
AcOH	65	35
HCOOH	15	85

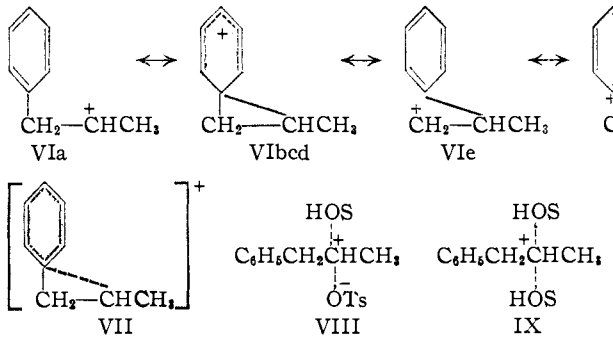
TABLE II

SUMMARY OF SOLVOLYSIS RATES

Compound	Solv.	Concn., M	Temp., °C.	k (sec.$^{-1}$)	$\Delta H^{\pm}$, kcal./mole	$\Delta S^{\pm}$, e.u.
$C_6H_5CH_2CH(OTs)CH_3$	EtOH	0.018-0.019	50.00	$(1.41 \pm 0.03) \times 10^{-6}$		
	AcOH		25.0[a]	1.50×10^{-8}		
	AcOH	.021-0.024	50.00	$(5.85 \pm 0.12) \times 10^{-7}$		
	AcOH	.025-0.032	74.81	$(1.31 \pm 0.02) \times 10^{-5}$	27.3	−2.7
	HCOOH	.076-0.084	25.12	$(1.37 \pm 0.03) \times 10^{-5}$		
$C_6H_5CH_2CHOBsCH_3$	AcOH		25.0[a]	7.25×10^{-8}		
	AcOH		49.60[a]	2.07×10^{-6}		
	AcOH	.026-0.030	75.01	$(3.90 \pm 0.08) \times 10^{-5}$	25.2	−6.6
	AcOH	.0261	99.67	$(4.52 \pm 0.17) \times 10^{-4}$		
	AcOH	.0283	99.79	$(4.74 \pm 0.09) \times 10^{-4}$		
	HCOOH	.082-0.090	24.96	$(3.01 \pm 0.03) \times 10^{-5}$		
p-$CH_3OC_6H_4CH_2CH(OTs)CH_3$	EtOH	.030	49.60	$(8.28 \pm 0.13) \times 10^{-6}$		
	AcOH		25.00[a]	4.85×10^{-7}		
	AcOH	.050	49.72	$(1.20 \pm 0.01) \times 10^{-5}$		
	AcOH	.050	74.76	$(1.94 \pm 0.03) \times 10^{-4}$	24.1	−6.4
	HCOOH	.05-0.07	25.12	$(5.1 \pm 0.5) \times 10^{-4}$		
$CH_3CH(C_6H_4$-OCH_3-$p)CH(OTs)CH_3$	AcOH	.040	49.74	$(1.87 \pm 0.02) \times 10^{-4}$		

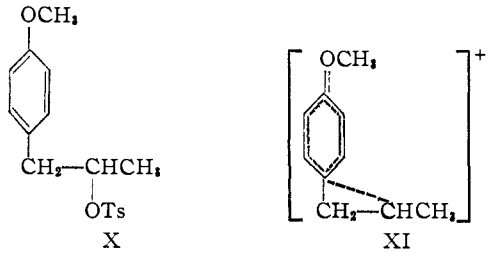
[a] Extrapolated from data at other temperatures.

terms of intermediate VII (contributing structures VIabcd; VIef less important) with over-all retention in the case of phenyl participation and intermediates VIII and IX with predominating inversion in the case of solvent participation. On this basis there are superimposed various proportions of over-all retention of configuration due to phenyl participation on the usual results in the various solvents. We do not know that the matter is this simple, and we hope later to understand this competition more fully.



In connection with the competition between neighboring phenyl and solvent participation, solvolysis rates were of interest, and Table II summarizes ethanolysis, acetolysis and formolysis rates of benzylmethylcarbinyl p-toluenesulfonate (III) and the corresponding p-bromobenzenesulfonate. The rate measurements were, for the most part, carried out by our conventional methods. In addition, the formolysis rate of benzylmethylcarbinyl p-toluenesulfonate(III), determined while we were still experimenting with methods[16] of determination of rate constants in formic acid, was also measured by a conductance method. Such a determination is illustrated in Fig. 2, where log $(C_\infty - C_0)/(C_\infty - C_t)$, with C representing observed conductance in ohms^{-1}, is plotted against time for formolysis in 0.01793 M solution at 24.9°. The rate constant of 1.40×10^{-5} sec.$^{-1}$ is in good agreement with the titrimetric value listed in Table II.

If the phenyl group is involved in participation in the rate-determining ionization, the energy of the transition state should be lowered, and the rate increased, by an electron-donating p-substituent, such as methoxyl, which will make the π-electrons of the phenyl group more available to the α-carbon atom. For this reason the solvolysis rates of the p-methoxy analog of III, p-methoxybenzylmethylcarbinyl p-toluenesulfonate (X) were of interest, and these are given in Table II. The necessary carbinol was prepared by reduction of p-anisylacetone which was derived from anethole by preparation and rearrangement of its epoxide.



Rate comparisons involving the p-methoxybenzylmethylcarbinyl (X), benzylmethylcarbinyl (III) and isopropyl esters are summarized in Table III on the basis of the rates in Table II and those previously reported for isopropyl p-bromobenzenesulfonate,[16,17,18] correcting for the difference[18] between a toluenesulfonate and a p-bromobenzenesulfonate where necessary. The right-hand half of the table gives the rate sequence EtOH:AcOH:HCOOH for each substance. The EtOH:AcOH comparison is at 50° except in the case of isopropyl p-bromobenzenesulfonate where it is at 70°. The AcOH:HCOOH comparison is at 25°. The left-

(16) Winstein and Marshall, THIS JOURNAL, **74**, 1120 (1952).

(17) Grunwald and Winstein, *ibid.*, **70**, 846 (1948).

(18) Winstein, *et al.*, *ibid.*, **74**, 1113 (1952).

TABLE III

RELATIVE SOLVOLYSIS RATES

	EtOH 50°	AcOH 50°	AcOH 25°	HCOOH 25°	EtOH	AcOH	HCOOH
H_3CO—C$_6$H$_4$—CH_2—$CHCH_3$	6	20.5	32	37	1	1.5	1500
C$_6$H$_5$—CH_2CHCH_3	1	1	1	1	2.4	1	415
CH_3CHCH_3	5	3.1	3.3	2	3.8	1	250

hand half of Table III compares, in different columns for each solvent, the rates of the three structures.

From Table III, it is clear that the introduction of the *p*-methoxy group is quite rate enhancing in acetic acid or formic acid as solvents, the factor being 37 in the latter solvent. This figure corresponds to a ρ in Hammett's $\rho\sigma$ treatment[19] of -5.8. While we are still exploring the quantitative aspects of the effect of substituents in participating and non-participating aryl groups, the indications are that the anisyl group of *p*-methoxybenzylmethylcarbinyl *p*-toluenesulfonate (X) is considerably involved in participation during solvolysis in acetic or formic acid as solvent (see XI). In fact, we can anticipate that, with X, retention of configuration will be the predominant steric result of solvolysis even in acetic acid.

The variation in the solvent sequence EtOH: AcOH:HCOOH, for isopropyl, benzylmethylcarbinyl and *p*-methoxybenzylmethylcarbinyl esters is interesting. With isopropyl the sequence is 3.8: 1:250. With benzylmethylcarbinyl it is 2.4:1:415. The rate of ethanolysis exceeds that of acetolysis by nearly as large a factor as in the case of isopropyl. Clearly ethanol is largely engaged in covalent attack[13] on carbon, competing extremely successfully with phenyl participation. The high extent of inversion in the steric result corresponds to this. With *p*-methoxybenzylmethylcarbinyl (X), the sequence is 1:1.5:1500, the tendency for the neighboring *p*-anisyl group to take over the back-side nucleophilic role being well-developed enough that ethanolysis is now below acetolysis in rate.[13]

It is interesting to compare the solvolysis rates of benzylmethylcarbinyl arylsulfonates, on the one hand, with isopropyl which does not involve participation, and, on the other, with *p*-methoxybenzylmethylcarbinyl which involves it more nearly over the whole solvent range. Thus we have $CH_3CHCH_3 > C_6H_5CH_2CHCH_3$ by a factor of 5 in ethanol, 3 in acetic acid and 2 in formic acid, the factor changing in the direction expected from an increasing contribution to the rate of benzylmethylcarbinyl from phenyl participation as we proceed from ethanol to formic acid. Similarly we have *p*-$CH_3OC_6H_4CH_2CHCH_3 > C_6H_5CH_2CHCH_3$ by a factor of 6 in ethanol, 20.5 in acetic acid at 50°, 32 in acetic acid at 25° and 37 in formic acid at 25°. Again the trend is in the proper direction for decreasing solvent participation in the benzylmethylcarbinyl case as we proceed from ethanol to formic acid.

(19) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 189.

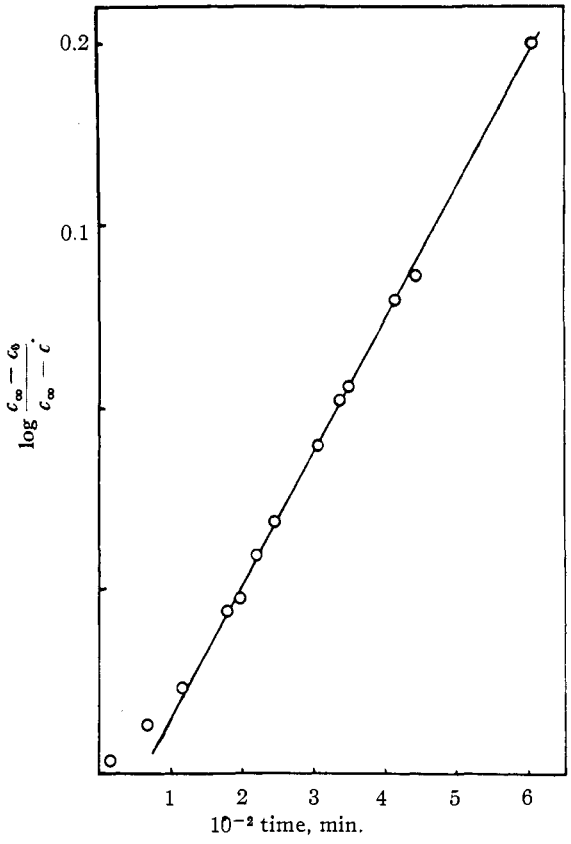
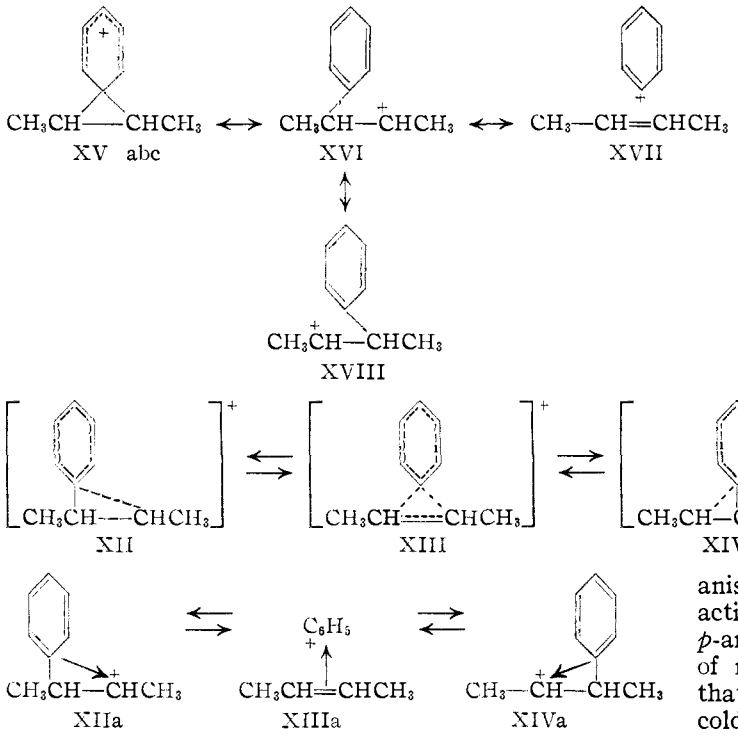


Fig. 2.—Determination of formolysis rate at 24.9° of 0.01793 *M* benzylmethylcarbinyl *p*-toluenesulfonate by conductance method.

The implications of the kind of control of stereochemistry of reactions displayed by neighboring phenyl in benzylmethylcarbinyl *p*-toluenesulfonate are numerous, but little is yet known regarding the scope and limitations of the phenomenon.

In properly substituted cases, just as in the case of neighboring vinyl,[2b] the above-discussed phenomenon of control of stereochemistry of substitution by neighboring aryl merges with the so-called Wagner–Meerwein phenomenon. A case in point is the 3-phenyl-2-butyl system recently reported by Cram.[20] In this system, with the additional β-methyl group to aid participation and hinder back-side solvent entry, neighboring phenyl achieves much more easily than in benzylmethylcarbinyl, nearly complete control of the stereochemical result of substitution. Even in acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate, roughly half the molecules of 3-phenyl-2-butyl acetate arise with retention of configuration and half the mole-

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

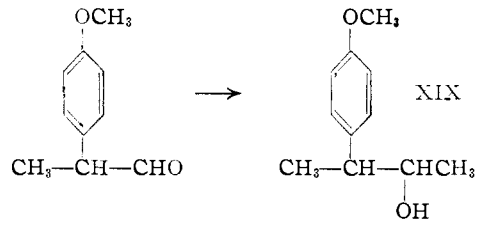


cules with Wagner–Meerwein rearrangement (C_6H_5 migration) and inversion both of C_α and C_β. Cram's most recent results[21] with this system can be expressed[22] in terms of a ratio of phenyl participation to solvent participation of *ca.* 12:1, clearly much larger than in the benzylmethylcarbinyl case.

Participation of the phenyl group in 3-phenyl-2-butyl brings about equivalence of C_α and C_β as illustrated in XII–XIV, it being not clear[25b] how many intermediate species require explicit mention. Dewar[23] type symbols corresponding to each of these species are also shown by XIIa–XIVa. The hybridization of orbitals on carbon in the benzene ring is favorable[24] to contribution of cyclopropane ring structures of the type XV to the hybrid species XIII with the central position for the phenyl.[25] There will also be contributions of other structures XVI–XVIII which are similar in type to those which are used to describe a bridged cation[26] with an aliphatic bridging group. The species XIII is an internal variety of the Pfeiffer–Wizinger[27] intermediate in electrophilic aromatic substitution, supported by the recent results on nitration[28] and bromination.[29]

The rate[18] of solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate is somewhat enhanced over that of benzylmethylcarbinyl by the β-methyl group. The rate of 3-phenyl-2-butyl *p*-toluenesulfonate is greater than that of benzylmethylcarbinyl *p*-toluenesulfonate by a factor of 4 in acetic acid at 50°, which extrapolates to a factor[30] of 5 at 25°. In formic acid where the rate-determining process for the two systems is more nearly similar, the factor for $CH_3CH(C_6H_5)CH(OTs)CH_3$: $C_6H_5CH_2CH(OTs)CH_3$ is 16 at 25°. Thus, again,[18] a β-methyl group is much more rate-enhancing when participation of the phenyl group is well enough developed than it is, for example, when introduced into isopropyl to give *s*-butyl (factor[18] of 2).

For determination of the effect on the solvolysis rate of the introduction of a *p*-methoxyl group into 3-phenyl-2-butyl *p*-toluenesulfonate, 3-*p*-anisyl-2-butanol (XIX) was prepared by the action of the methyl Grignard reagent on α-*p*-anisylpropionaldehyde. A mixture of a pair of racemates is produced, Sosa[31] reporting that, when 3-*p*-anisyl-2-butanol stands in the cold for a period of several months, a solid diastereomer crystallizes out. In the present work the solid racemate was obtained through the acid phthalate. In view of the near identity of solvolysis rates[18] of the two racemic 3-phenyl-2-butyl *p*-toluenesulfonates, it was deemed sufficient, for studying the effect of *p*-methoxyl on rate, to measure the rate of solvolysis of only one of the *p*-methoxyl substituted racemic *p*-toluenesulfonates, the ester from the solid racemic carbinol.



The acetolysis of 3-*p*-anisyl-2-butyl *p*-toluenesulfonate, followed to 97% completion, yielded an excellent first-order rate constant of 1.87 ± 0.02 × 10^{-4} sec.$^{-1}$ at 49.74° (Table II). Thus the rate comparison: $CH_3CH(C_6H_4OCH_3\text{-}p)CH(OTs)CH_3$, 79 > $CH_3CH(C_6H_5)CH(OTs)CH_3$, 1; is obtained, the effect of a *p*-methoxyl group being more serious here than for the benzylmethylcarbinyl system. The observed factor corresponds to a Hammett ρ of −7.1. Comparing the two *p*-methoxy-substituted cases, the factor due to a β-methyl group is again 16.

We point out elsewhere[32] the possible analogy between the excited state in light absorption of unsaturated materials having a vinyl group in the 2-position and the transition state for ionization of a γ-unsaturated alkyl halide or *p*-toluenesulfo-

(21) Cram, THIS JOURNAL, in press.

(22) Winstein and Schreiber, *ibid.*, in press.

(23) Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949, p. 212.

(24) (a) Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (b) Coulson and Moffitt, *Phil. Mag.*, [7] **30**, 1 (1949).

(25) The Dewar symbol XIIIa tends to obscure the fact that the phenyl group is playing heavily the role of an electron source.

(26) Winstein and Morse, THIS JOURNAL, **74**, 1133 (1952).

(27) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

(28) Melander, *Acta Chem. Scand.*, **3**, 95 (1949); (b) Gillespie, Hughes, Ingold, Millen and Reed, *Nature*, **163**, 599 (1949).

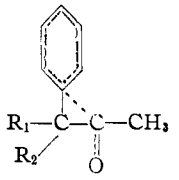
(29) Melander, *Arkiv Kemi*, **2**, 213 (1950).

(30) These comparisons may be complicated by extra disturbances, such as "internal return," which, however, have become quite unimportant in formic acid as a solvent.[21]

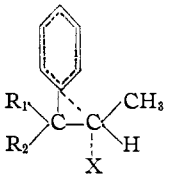
(31) Sosa, *Ann. Chim.*, [11] **14**, 5 (1940).

(32) Winstein and Schlesinger, being submitted to THIS JOURNAL.

nate. This analogy carries over when the vinyl group is replaced by aryl as shown in XX and XXI.



XX



XXI

While it is not yet clear what degree of correspondence there should be between effects on the ultraviolet spectrum of ketones (XX) and effects on reactivity of *p*-toluenesulfonates (XXI) or on the stereochemical outcome of the solvolyses, it is of interest to see what correlation there is between the phenomena. For α-phenyl ketones Kumler[33] has reported a characteristic band in the ultraviolet spectrum at *ca.* 295 mμ with an extinction coefficient more than tenfold that of a simple aliphatic carbonyl compound. This has been observed for $R_1 = R_2 = CH_3$; $R_1 = CH_3$, $R_2 = H$; $R_1 = R_2 =$ H in XX, while for the analogous *p*-toluenesulfonates XXI, there is observed a rate enhancement for $R_1 = R_2 = CH_3$ and control of stereochemistry by neighboring phenyl for $R_1 = CH_3$, $R_2 = H$ and $R_1 = R_2 = H$. Further, with α-phenylcyclohexanone the band at 295 mμ is of very low intensity, while with *trans*-2-phenylcyclohexyl *p*-bromobenzenesulfonate[34] the net effect on rate of the phenyl group is more rate-retarding than in 3-phenyl-2-butyl *p*-toluenesulfonate.

Experimental

***dl*-Benzylmethylcarbinol and Derivatives.**—The carbinol b.p. 97% (10.5 mm.), was prepared either by the action of methylmagnesium iodide on phenylacetaldehyde or by reduction of phenylacetone with lithium aluminum hydride. Treatment with phthalic anhydride in pyridine on the steam-bath for 4.5 hours and working up in the usual way yielded acid phthalate, m.p. 113–113.5° (reported 113–114°)[35] in 76–79% yield. The *dl*-toluenesulfonate, m.p. 93.7–94° (reported[11] 94°) was obtained in the usual manner. Similarly the *dl*-*p*-bromobenzenesulfonate, m.p. 80–81°, was prepared in 75% yield.

Anal. Calcd. for $C_{15}H_{15}O_3SBr$: C, 50.71; H, 4.26. Found: C, 50.65; H, 4.34.

Preparation of *dl*-Benzylmethylcarbinyl Formate.—A mixture of *dl*-benzylmethylcarbinol (30 g., 0.22 mole), formic acid (200 cc., Baker and Adamson, 98%) and anhydrous copper sulfate (40 g., 0.25 mole) was heated at 98° for 24 hours. The cooled solution was poured into water (200 cc.) and extracted with 200 ml. of Skellysolve B (ligroin, b.p. 63–70°). The aqueous layer was extracted twice more with Skellysolve B. The combined organic layers were neutralized, washed with water and dried with anhydrous potassium carbonate. After removing the solvent by distillation on the steam-bath, the residue was distilled under reduced pressure to yield 26 g., 72%, of material, b.p. 63–64.5° (1 mm.). Fractionation gave an analytical sample, b.p. 68° (1.6 mm.), $n^{25}D$ 1.4974, d^{25}_4 1.025 (reported b.p. 108–110° (19 mm.), $n^{24.5}D$ 1.4975, d^{22}_4 1.027).[36]

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.29; H, 7.36.

Active Benzylmethylcarbinol and Derivatives.—Benzylmethylcarbinol was resolved by the method of Pickard and Kenyon,[35] the samples used in this work being: (1) $n^{25}D$ 1.5181, $\alpha^{23}D$ +26.81° (1 dcm.), $[\alpha]^{23}D$ +27.05°; (2) $n^{25}D$ 1.5182, $\alpha^{27}D$ +26.70°, $[\alpha]^{27}D$ +27.0° (reported $[\alpha]^{20}D$ 26.55°, $[\alpha]^{20}D$ 28.3°)[11,37]; (3) $n^{20}D$ 1.5201, $\alpha^{27}D$ −19.84°; (4) $n^{25}D$ 1.5182, $\alpha^{27}D$ −17.57°; (5) $\alpha^{25}D$ +26.87°.

The (+)-alcohol sample (I) gave a *p*-toluenesulfonate, $[\alpha]^{25}D$ +23.33°, $\alpha^{25}D$ +3.70° ($CHCl_3$, *c* 15.86) (reported by Phillips $[\alpha]D$ 24.97°), the (+)-alcohol sample, (2) a *p*-toluenesulfonate, m.p. 71–72°, $[\alpha]^{26}D$ +26.1° (benzene, *c* 17.1) (reported $[\alpha]D$ 27.85°), the (−)-alcohol sample, (3) a *p*-toluenesulfonate, m.p. 72–80°, $[\alpha]^{24.5}D$ −20.4° (benzene, *c* 16.9), the (−)-alcohol sample, (4) a *p*-toluenesulfonate, m.p. 76–80°, $[\alpha]^{24.5}D$ −15.5° (benzene, *c* 17.0), and the (+)-alcohol sample, (5) a *p*-toluenesulfonate, $[\alpha]^{25}D$ 24.51° ($CHCl_3$, *c* 16.4).

The (+)-alcohol sample (2) yielded, on treatment with acetic anhydride, an acetate, b.p. 111° (14 mm.), $n^{25}D$ 1.4867, $\alpha^{24.5}D$ 5.51° (1 dcm.).

Acetolysis of Benzylmethylcarbinyl *p*-Toluenesulfonates.—The *dl*-toluenesulfonate (30.0 g., 0.103 mole) was dissolved in 1030 ml. of glacial acetic acid, m.p. 16.3°, and the solution was held at *ca.* 100° for 48 hours. Then it was cooled and poured with stirring into excess potassium carbonate solution. The product was extracted with ether, the ether was distilled, and the residue was saponified with alcoholic sodium hydroxide. Dilution with water, extraction with ether, drying of the extract over Drierite and distillation yielded benzylmethylcarbinol, b.p. 97° (10.5 mm.), in 49% yield. From a one-gram sample of the carbinol was obtained acid phthalate, m.p. and mixed m.p. 113.5–114.5°, in 67% yield.

Analogous treatment of the toluenesulfonate of the (−)-alcohol sample (3) gave rise to a 60% recovery of (+)-alcohol, b.p. 97° (10.5 mm.), $n^{20}D$ 1.5210, $\alpha^{26}D$ +5.79° (1 dcm.).

(+)-Benzylmethylcarbinyl acetate, $\alpha^{24.5}D$ +5.51° (1 dcm.) (15.0 g.) was heated at 100° for 48 hours in 842 ml. of glacial acetic acid, m.p. 16.3°, which was made 0.07 *M* in *p*-toluenesulfonic acid. Working up in the usual way gave a 57% recovery of acetate, b.p. 110° (14 mm.), $n^{25}D$ 1.4871, $\alpha^{24.5}D$ +5.8°.

Formolysis of Ethyl *p*-Toluenesulfonate.—A solution of 10 g., 0.05 mole, of recrystallized Eastman Kodak Co. ethyl *p*-toluenesulfonate, m.p. 32.5–33.0°, in formic acid (250 cc., Baker and Adamson 98–100%) was heated at 78° for 48 hours. The formic acid as well as lower boiling products were distilled on the steam-bath under reduced pressure. Drying of semi-solid residue over phosphorus pentoxide under reduced pressure (0.9 mm.) for four hours yielded 8.15 g. of slightly yellow material, m.p. 103.5–104.5°, mixed m.p. with *p*-toluenesulfonic acid monohydrate 103.5–105°. Conversion of the material to acid chloride[38] gave, in 78% yield, *p*-toluenesulfonyl chloride, m.p. and mixed m.p. with authentic material, 68–69°.

Formolysis of Benzylmethylcarbinyl *p*-Toluenesulfonate. Isolation of *p*-Toluenesulfonic Acid.—A solution of benzylmethylcarbinyl toluenesulfonate (24.5 g., 0.085 mole) in formic acid (500 cc., Baker and Adamson, 98–100%) was heated for 18 hours at 80°. The formic acid, as well as the volatile product, was distilled under reduced pressure on the steam-bath. The residue, which nearly completely solidified, was filtered to yield 14.4 g. (89%) of a solid, m.p. 90.5–91.5°, which was not purified, but was treated with a threefold excess of thionyl chloride. By recrystallization there was obtained 10.9 g., 0.057 mole (67% yield from starting toluenesulfonate) of *p*-toluenesulfonyl chloride, m.p. 67–68°, mixed m.p. with authentic material, 67.2–68.5°.

Formolysis of *dl*-Benzylmethylcarbinyl Toluenesulfonate.—A solution of 29.0 g. (0.1 mole) of *dl*-benzylmethylcarbinyl toluenesulfonate and 5 g. (0.05 mole) of sodium carbonate in 1 liter of formic acid (C.P., Baker and Adamson, 98–100%) was heated at 79–81° for 21 hours. The cooled solution was poured into a mixture of water and Skellysolve B. The aqueous layer was twice more extracted with Skellysolve B. The solvent was then distilled from the combined organic layers. To the residue in ethanol (150 cc., 95%) was added sodium hydroxide (18 g., 0.45 mole) and the solution refluxed for one hour. After the reaction mixture was poured into 250 cc. of water and extracted with ether, the organic layer was dried with sodium sulfate.

(33) (a) Kumler, Strait and Alpen, THIS JOURNAL, **72**, 1463 (1950); (b) Alpen, Kumler and Strait, *ibid.*, **72**, 4558 (1950).

(34) E. Grunwald, Ph.D. Thesis, U. C. L. A., 1947.

(35) Pickard and Kenyon, *J. Chem. Soc.*, **105**, 1115 (1914).

(36) Pickard, *et al.*, *ibid.*, **123**, 1 (1923).

(37) Levene and Stevens, *J. Biol. Chem.*, **89**, 471 (1930).

(38) Shriner and Fuson, "The Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., p. 216.

Following the distillation of the ether on the steam-bath, the residue was fractioned under reduced pressure through a 30-cm. center-rod column to yield 6.5 g., 48%, of a center cut, b.p. 96–98° (12 mm.), $n^{25}D$ 1.5191, acid phthalate, m.p.113°.

Formolysis of *dl*-Benzylmethylcarbinyl Toluenesulfonate. Isolation of Formate.—A solution of 86.0 g. (0.297 mole) of *dl*-benzylmethylcarbinyl toluenesulfonate and sodium carbonate (17 g., 0.16 mole) in formic acid (1 liter, 98–100%) was heated for 36 hours at 78–80°. The cooled solution was poured into Skellysolve B (1 liter, redistilled b.p. 64–70°) and the resulting mixture washed with water (one 1-liter portion and two 500-cc. portions). The first water washing was extracted with one 250-cc. portion of Skellysolve B. The combined Skellysolve layers were shaken with aqueous sodium carbonate and dried over potassium carbonate. The Skellysolve was distilled through a 60-cm. glass helices packed column at a reflux ratio of 10:1, and the residue was fractionated through a 38-cm. center-rod column at 11 mm. The fractions obtained were: (1) 0.5 g., b.p. 57–91°; (2) 1.0 g., b.p. 92–96°; (3) 33.8 g., b.p. 96–97°, $n^{25}D$ 1.4973, d^{25}_4 1.024; residue 3.5 g. The second and third fractions represent a 72% yield of *dl*-benzylmethylcarbinyl formate. Saponification of part of fraction (3) gave carbinol, $n^{25}D$ 1.5192.

Formolysis of (+)-Benzylmethylcarbinyl *p*-Toluenesulfonate.—A solution of 25.1 g., 0.086 mole, of tosylate, $[\alpha]^{25}D$ +23.33 ($CHCl_3$) and 5.3 g., 0.05 mole, sodium carbonate in 500 ml. of Baker and Adamson C.P. 98–100% formic acid was heated at 75–81° for 17 hours and worked up as in the case of the *dl*-tosylate. There was obtained 8.9 g., 80%, benzylmethylcarbinyl formate, b.p. 92–93° (12 mm.), $n^{25}D$ 1.4973, $\alpha^{22}D$ −5.30° (1 dcm.), $[\alpha]^{22}D$ −5.17°. The formate was hydrolyzed with potassium hydroxide (4.4 g., 0.08 mole) in 100 ml. of absolute methanol by heating on a steam-bath for two hours. The mixture was then poured into 300 cc. of water and extracted thrice with ether. After drying over magnesium sulfate, the ether was removed at atmospheric pressure and the residue distilled under reduced pressure, yielding 5.2 g., 70% of (+)-benzylmethylcarbinol, b.p. 72° (4 mm.), $\alpha^{23}D$ +17.91° (1 dcm.), $[\alpha]^{23}D$ +18.07°.

The formolysis was also carried out on 21.5 g., 0.0741 mole, of the *p*-toluenesulfonate of (−)-alcohol sample (4), by heating at 80° for 19 hours in 750 ml. of formic acid (0.1 *M* solution) containing no sodium formate. Working up the reaction mixture in the usual way and saponification of the formate yielded carbinol in 40% yield, b.p. 97° (10.5 mm.), $n^{25}D$ 1.5182, $\alpha^{24.5}D$ −5.22° (1 dcm.).

Formolysis of 25.2 g. (0.086 mole) of the toluenesulfonate of (+)-alcohol (5) in 1 liter specially dried 99.8% formic acid containing 5.4 g. (0.05 mole) of anhydrous sodium carbonate for seven hours at 50° and 11 hours at room temperature, isolation of the formate and saponification in the usual way gave the benzylmethylcarbinol in three fractions: I, 2.1 g., b.p. 93–95° (10–11 mm.), $n^{25}D$ 1.5195; II, 5.6 g., b.p. 95.5–97° (10–11 mm.), $n^{25}D$ 1.5192; III, 1.8 g., b.p. 97–98° (10–11 mm.) $n^{25}D$ 1.5187. The yield of carbinol was 81% and the rotation of fraction II given by $\alpha^{25}D$ +18.79°.

***p*-Methoxybenzylmethylcarbinol and Derivatives.**—A mixture of 450 ml. (3 moles) of technical anethole, 535 g. (3 moles) of N-bromosuccinimide and 3 l. of water was stirred with cooling for two hours, then saturated with sodium chloride and extracted with ether. To the ether extract, dried over potassium carbonate, was added slowly with cooling 180 g. (4.5 moles) of powdered C.P. sodium hydroxide. After the addition was complete, the reaction mixture was stirred at room temperature for eight hours. The ether solution obtained by addition of 500 ml. of water to the reaction mixture and extraction of the aqueous layer with ether, was washed with water and dried over Drierite. To the cooled residue, remaining after evaporation of the ether, 1 g. of *p*-toluenesulfonic acid monohydrate was added; the solution was very carefully warmed with continuous stirring and, as soon as the reaction started, submerged in a salt–ice-bath. The black oil that formed was distilled under reduced pressure, yielding 169 g. (40%) of *p*-anisylacetone (light yellow), b.p. 134–137° (12 mm.) (reported 136–138°),[39] $n^{25}D$ 1.5270 (reported $n^{20}D$ 1.5253),[39] oxime, m.p. 77.5–78.0° (reported m.p. 78–79°).[40] The substitution of 1 g. of magnesium iodide for the toluenesulfonic acid, gave a 38% yield of anisylacetone.

The anisylacetone was reduced in 75% yield with lithium aluminum hydride by the usual method[41] to *p*-methoxybenzylmethylcarbinol, b.p. 119° (4 mm.), $n^{25}D$ 1.5261.

The *p*-methoxybenzylmethylcarbinyl hydrogen phthalate, m.p. 83.1–83.2°, after three recrystallizations from benzene–Skellysolve B, was prepared by the pyridine–phthalic anhydride method.

Anal. Calcd. for $C_{18}H_{18}O_5$: C, 68.79; H, 5.77. Found: C, 68.71; H, 5.86.

The *p*-methoxybenzylmethylcarbinyl acetate, b.p. 113° (1.7 mm.), $n^{25}D$ 1.4989, was prepared in the usual manner in 71% yield from 32 g. (0.2 mole) of alcohol, 21 g. (0.21 mole) of acetic anhydride and 5 ml. of pyridine.

Anal. Calcd. for $C_{12}H_{16}O$: C, 69.20; H, 7.74. Found: C, 68.94; H, 7.97.

The *p*-methoxybenzylmethylcarbinyl *p*-toluenesulfonate, m.p. 80.0°, after two recrystallizations from Skellysolve B, equiv. wt. in acetolysis, 322.7 (calcd. 320.4), was obtained in 80% yield from 10 g. (0.06 mole) carbinol and 11.5 g. (0.06 mole) *p*-toluenesulfonyl chloride in 10 ml. of pyridine, allowing the reaction mixture to stand overnight at room temperature and working up in the usual manner.

Anal. Calcd. for $C_{17}H_{20}SO_4$: C, 63.73; H, 6.29. Found: C, 63.90; H, 6.33.

Acetolysis of *p*-Methoxybenzylmethylcarbinyl *p*-Toluenesulfonate.—A solution of 80 g. (0.25 mole) of *p*-methoxybenzylmethylcarbinyl *p*-toluenesulfonate and 14 g. (0.13 mole) of sodium carbonate in 2 l. of 99.5% acetic acid was heated for 18 hours at 77–81°. The combined Skellysolve layers, obtained by pouring the reaction mixture into 2 l. of Skellysolve B and washing with water (one 1-l. and two 500-ml. portions) and then extracting the aqueous washings once with 500 ml. of Skellysolve B, was neutralized with 5% potassium carbonate solution and dried over potassium carbonate. After distilling the Skellysolve through a 60-cm. glass helix column, the residue was distilled *in vacuo* yielding 17.1 g. (34%) of *p*-methoxybenzylmethylcarbinyl acetate, b.p. 127° (4 mm.), $n^{25}D$ 1.4990, which on hydrolysis and esterification with phthalic anhydride gave a phthalate, m.p. 82.5–83.2°, and 6.9 g. boiler residue, which may represent anethole polymer.

In a control run of the extraction procedure, using 20 g. of *p*-methoxybenzylmethylcarbinyl acetate and 15 g. of anethole, a 37% recovery of acetate and 61% recovery of anethole was obtained.

α-*p*-Anisylpropionaldehyde was prepared by the method of Bougault[31,42,43] in 47% yield, b.p. mainly 108–111° (5 mm.), $n^{25}D$ 1.5257 (reported[31] $n^{20}D$ 1.5271).

3-*p*-Anisyl-2-butanol.[31]—A Grignard solution was prepared from 8 g. of magnesium turnings in 400 ml. of anhydrous ether and 56 g. of methyl iodide. The solution was cooled to −15° and 53.9 g. (0.328 mole) of α-*p*-anisylpropionaldehyde in an equal volume of anhydrous ether was added dropwise, with continuous stirring, the temperature of the reaction mixture being maintained at −10 to −15°. Stirring was continued for 10 minutes at room temperature and 10 minutes at 50°, and the reaction mixture was worked up in the usual way. Distillation through a 4-in. Vigreux column yielded 43.4 g. (73.5%) of material, b.p. 109–120° (3.5 mm.).

3-*p*-Anisyl-2-butyl Hydrogen Phthalate.—One gram of crude 3-*p*-anisyl-2-butanol was converted to acid phthalate by treatment with phthalic anhydride and pyridine on the steam-bath overnight. The crude yellow product was recrystallized from a Skellysolve B–benzene mixture to yield 0.40 g. (22%) of material, m.p. 127.8–129.0°. After four more recrystallizations, a constant melting point of 136.5° was obtained.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.49; H, 6.14. Found: C, 69.34; H, 6.28.

From 42.2 g. of crude 3-*p*-anisyl-2-butanol was obtained 16.1 g. (21%) of acid phthalate. This material was added to 300 ml. of 30% aqueous sodium hydroxide and the carbinol product was removed by steam distillation. The cooled distillate was filtered and the waxy white crystals

(39) Horing, *Ber.*, **38**, 3479 (1905).

(40) Wallach and Muller, *Ann.*, **332**, 3231 (1904).

(41) Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

(42) Bougalt, *Bull. soc. chim.*, [3] **25**, 447 (1901).

(43) Bougalt, *Ann. chim.*, [7] **25**, 515 (1902).

dried in vacuum to yield 5.2 g. (59%) of 3-*p*-anisyl-2-butanol, m.p. 58.8–59.2° (reported[31] 60° for the solid diastereoisomer).

3-*p*-Anisyl-2-butyl *p*-Toluenesulfonate.—4.0 g. (0.022 mole) of 3-*p*-anisyl-2-butanol was dissolved in 4.0 ml. of dry pyridine. The solution was cooled in ice, 4.3 g. (0.022 mole) of recrystallized *p*-toluenesulfonyl chloride, m.p. 68.5–69.0°, was added, and the mixture swirled in an ice-bath until the chloride dissolved. The mixture was allowed to stand overnight and then it was worked up in the conventional way. The bulk of the oily product was recrystallized from a dry ether–light petroleum mixture in a Dry Ice–acetone-bath, with the aid of seed crystals obtained by trituration of some of the oil with low-boiling pet. ether at −80°. There was obtained 4.2 g. (55%) of white product in several crops: seed crystals, m.p. 47.0–47.3°; 1st crop, m.p. 43.0—43.4°; 2nd crop, m.p. 43.0–45.0°; 3rd and 4th crops, more crude and sticky. The first crop was used almost immediately for rate determinations. The second crop of crystals was recrystallized from ether–petroleum ether in an attempt to obtain an analytical sample. A carbon and hydrogen analysis on some of the product, m.p. 48.5–50.0°, mixed m.p. with 3-*p*-anisyl-2-butanol 41–53°, was still poor. The *p*-toluenesulfonate used for acetolysis gave an infinity equivalent weight of 420.6 (calcd. 334.4).

Kinetic Measurements.—The procedures for determination of solvolysis rates in acetolysis,[44] ethanolysis,[13] and formolysis[16] were those previously described. The formic acid solvent contained 0.19% water by Karl Fischer titration and 99.95% acid by base titration. In ethanolysis and acetolysis the reactions were followed to 70–90% completion. This was true also in formolysis, except in the case of benzylmethylcarbinyl *p*-bromobenzenesulfonate whose reaction was followed to 40% completion. First order rate constants (Table II) were very satisfactory except in formolysis of *p*-methoxybenzylmethylcarbinyl *p*-toluenesulfonate where the mean deviation was higher (Table II) and a general downward drift in rate constant was apparent.

The formolysis rate of benzylmethylcarbinyl *p*-toluenesulfonate was also measured from the rate of increase of the conductance of a 0.01793 *M* solution of the ester as measured in a conductance cell with smooth platinum electrodes, using an impedance bridge (type 650-A, General Radio Co., Cambridge, Mass.) to measure resistance.

(44) Winstein, Grunwald and Ingraham, THIS JOURNAL, **70**, 821 (1948).

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

Neighboring Carbon and Hydrogen. X. Solvolysis of *endo*-Norbornyl Arylsulfonates[1,2,3]

BY S. WINSTEIN AND D. TRIFAN

Solvolysis of *endo*-norbornyl arylsulfonates proceeds in glacial acetic acid, aqueous acetone and aqueous dioxane to give completely the corresponding *exo*-derivative. That this *endo* to *exo* change involves rearrangement is clear from the complete resolution of *endo*-norbornyl alcohol and the solvolysis of optically active *endo*-norbornyl *p*-bromobenzenesulfonate in glacial acetic acid, ethanol and 75% aqueous acetone. Nearly complete loss of activity attends the formation of *exo*-products, first-order polarimetric rate constants agreeing with titrimetric rate constants within experimental error. The facts are most simply explained with carbon migration in the norbornyl cation. While the geometry in the *endo*-norbornyl *p*-bromobenzenesulfonate is unfavorable to participation of the C_1–C_6 bonding electron cloud in the ionization process, ionization is, for the most part, followed by rearrangement to the presumably more stable bridged structure. Solvent intervention, with 7–8% inversion, competes with carbon migration in acetolysis.

Among the norbornyl derivatives, the *exo*-configuration is the one associated with an enhanced rate of solvolysis.[3,4] Also, as reported previously in preliminary form[3] and in detail in the following paper,[5] the indications from stereochemical scrutiny of the solvolysis are that solvolysis proceeds with Wagner–Meerwein rearrangement. It would be instructive to know whether with the *endo* configuration, which is not associated with an enhanced solvolysis rate, rearrangement nevertheless accompanies solvolysis. The use of optically active *endo*-norbornyl derivatives represents one of the approaches to this problem, and, in this paper, we report the study of the solvolysis of *dl* and resolved *endo*-norbornyl arylsulfonates.

endo-Dehydronorbornyl acetate was prepared from cyclopentadiene and vinyl acetate with only slight modification of the method of Alder and Rickert.[6] Hydrogenation[6] of this material gave *endo*-norborneol (I) but this material was clearly not homogeneous, the Diels–Alder reaction being not completely stereospecific as was also noted recently by Roberts and co-workers.[7] The crude acid phthalate was a mixture and the crude toluenesulfonate (III, X = *p*-CH_3) was contaminated with material which solvolyzed much more rapidly than the *endo*-*p*-toluenesulfonate.

Solvolysis of the crude *endo*-*p*-toluenesulfonate (III) gave rise to products at least very largely *exo*. Thus acetolysis in glacial acetic acid gives acetate product IV (obtainable in 86% yield) which is at least largely *exo* as shown by comparison of the infrared spectrum of the acetolysis product (Fig. 1) with those of *endo*-norbornyl acetate (Fig. 1) and *exo*-norbornyl acetate.[5] Treatment of the acetate with lithium aluminum hydride and conversion of the carbinol product to 3,5-dinitrobenzoate gave 3,5-dinitrobenzoate of *exo*-norborneol (II) with no evidence of contamination with the *endo*-isomer. Similarly, hydrolysis in aqueous dioxane or aqueous acetone yielded *exo*-norborneol (II) either as the 3,5-dinitrobenzoate or as the acid phthalate in yields of 76–78% with no evidence for the presence of *endo*-isomer in the product. The results of solvolysis of pure *endo*-

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(2) Much of the material of this paper was presented in summary: (a) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of Abstracts; (b) at Montpellier, France, April, 26, 1950, *Bull. soc. chim.*, [5] **18**, C55 (1951); (c) presented before Organic Division of American Chemical Society, Boston, Mass., April 2–5, 1951, page 54M of Abstracts.

(3) Preliminary communication, Winstein and Trifan, THIS JOURNAL, **71**, 2953 (1949).

(4) Winstein, Morse, Grunwald, Jones, Corse and Marshall, *ibid.*, **74**, 1127 (1952).

(5) Winstein and Trifan, *ibid.*, **74**, 1154 (1952).

(6) Alder and Rickert, *Ann.*, **543**, 1 (1940).

(7) Roberts, *et al.*, THIS JOURNAL, **72**, 3116 (1950).