

**Preparation of 4-Methylcyclohexanone from 4-Methylcyclohexylamine.**—A solution of 1.13 g. (0.01 mole) of the amine, 1 ml. of concentrated hydrochloric acid, 2 ml. of glacial acetic acid and 2 ml. of water was cooled to 0°. With stirring, a solution of 2.6 g. (0.03 mole) of sodium nitrite in 5 ml. of water was added dropwise. The reaction mixture was stirred for 10 minutes. The brown organic layer was separated and the aqueous layer was extracted with two 2-ml. portions of ether, the extracts being added to the organic layer.

The combined organic layer was added to a solution of 0.76 g. (0.0019 mole) of potassium dichromate, 0.42 ml. (0.015 mole) of concentrated sulfuric acid and 2.5 ml. of water. This mixture was stirred and heated at 75–80° for four hours. Ten milliliters of water was added and the mixture was distilled until clear distillate came over. The distillate was extracted with two 2-ml. portions of ether. The extracts were dried over anhydrous magnesium sulfate and the ether was evaporated by a stream of dried air. There remained 0.30 g. of 4-methylcyclohexanone as a yellow oil

(semicarbazone m.p. 185–190°, lit.<sup>31</sup> m.p. 192–193°). The dinitrophenylhydrazone of the yellow oil was prepared by dissolving the balance of the oil in 10 ml. of ethanol and adding it to 20 ml. of 2,4-dinitrophenylhydrazine solution. The solid which precipitated was filtered and recrystallized from petroleum ether. It melted at 109–116°. Four recrystallizations from ethanol and water, using the second crop of crystals from each recrystallization, gave a product which melted at 128–131°. The melting point of the dinitrophenylhydrazone of 4-methylcyclohexanone has been reported as 130°,<sup>32</sup> 116°<sup>33</sup> and 134.7–135.1°.<sup>34</sup>

(31) H. E. Ungnade and A. D. McLaren, *J. Org. Chem.*, **10**, 29 (1945).

(32) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," third ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

(33) M. Metayer and S. Roumens, *Compt. rend.*, **225**, 1324 (1947).

(34) H. Adkins and A. G. Rossow, *THIS JOURNAL*, **71**, 3830 (1949).  
NEW ORLEANS, LA.

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

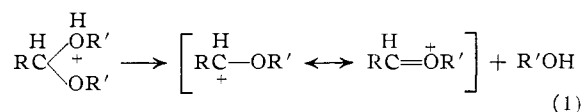
## The Hydrolysis of Acetals of Methylvinylcarbinol, Phenylvinylcarbinol and $\alpha$ -Phenylethyl Alcohol

BY JOHN D. DRUMHELLER<sup>1</sup> AND LAWRENCE J. ANDREWS

RECEIVED JANUARY 26, 1955

The acetals of methylvinylcarbinol, phenylvinylcarbinol and (–)- $\alpha$ -phenylethyl alcohol have been synthesized. The first two are formed without allylic rearrangement, and the asymmetric centers of the third have the configuration of the parent alcohol. The acid-catalyzed hydrolysis of methylvinylcarbinyl acetal occurs without allylic rearrangement, and that of (–)- $\alpha$ -phenylethyl alcohol takes place with complete retention of configuration at the asymmetric centers. The cinnamyl alcohol which forms during the hydrolysis of phenylvinylcarbinyl acetal is produced from isomerization of phenylvinylcarbinol, which is the immediate reaction product. Apparently no O–R' bond fission occurs during the hydrolysis of the three acetals [RCH(OR')<sub>2</sub>], even though derivatives of these alcohols (R'OH) usually undergo solvolysis through the formation of R' carbonium ion intermediates.

The slow step in the acid-catalyzed hydrolysis of the acetal of an aliphatic alcohol is generally depicted<sup>2</sup> as a unimolecular dissociation (1) of the conjugate acid of the acetal.



Subsequent rapid reaction of the highly resonance stabilized cation with water to form the hemiacetal, which then decomposes by a path analogous to (1), is presumed to lead to formation of the aldehyde. This mechanism is reasonable in the light of early work<sup>3</sup> on the effects of changes in acetal structure on the hydrolysis rate. The recent observation<sup>4</sup> that the logarithm of the hydrolysis rate constant of methylal is a linear function of the acidity function of the medium strongly supports the contention that step (1) is rate determining.

It is also significant that the process of formation and subsequent hydrolysis of a simple acetal is accomplished by complete retention of configuration at the carbinol carbon of the alcohol.<sup>5–7</sup> This ob-

ervation eliminates the possibility that R' carbonium ion is formed as a reaction intermediate in the cases cited. It is conceivable that certain acetals, prepared from alcohols the derivatives of which readily undergo SN1 type displacements, may hydrolyze by the R' carbonium ion path rather than by route (1).<sup>8</sup> The possibility has now been explored that this abnormal cleavage process might be operative during hydrolysis of acetals of methylvinylcarbinol, phenylvinylcarbinol and (–)- $\alpha$ -phenylethyl alcohol.<sup>9</sup> In all three cases it appears that the normal hydrolysis path of equation (1) is preferred.

**Preparation and Hydrolysis of the Acetals.**—The three acetals were prepared from the reaction of acetaldehyde and the appropriate alcohol in the presence of calcium chloride with hydrogen chloride as a catalyst. That allylic configuration was maintained in the formation of methylvinylcarbinyl acetal was established through catalytic hydrogenation of the unsaturated product. The reduced acetal was identical in physical properties with those of a known sample of *sec*-butyl acetal and produced *sec*-butyl alcohol as its only alcoholic hydrolysis product.

(1) Organic Chemicals Department, E. I. du Pont de Nemours and Co., Jackson Laboratory, Wilmington, Del.

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334.

(3) A. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **122**, 349 (1926).

(4) D. McIntyre and F. A. Long, *THIS JOURNAL*, **76**, 3240 (1954).

(5) H. K. Garner and H. J. Lucas, *ibid.*, **72**, 5497 (1950).

(6) J. M. O'Gorman and H. J. Lucas, *ibid.*, **72**, 5489 (1950).

(7) E. M. Alexander, H. M. Bursch and G. L. Webster, *ibid.*, **74**, 3173 (1952).

(8) Although the acetone ketals of the *cis*-1,2-diols of tetrahydronaphthalene, hydrindene and 1-phenylcyclohexane appear to be likely candidates for such abnormal hydrolytic cleavage at the 1-position, the *trans*-diols have been isolated only as small fractions of the total glycols obtained on hydrolysis. The *trans*-diols are presumed to form by a glycol isomerization following ketal hydrolysis; cf. J. Böeseken and H. Derx, *Rec. trav. chim.*, **40**, 519 (1921); J. Böeseken, *Ber.*, **56B**, 2409 (1923); P. H. Hermans, *ibid.*, **57B**, 824 (1924).

(9) Esters of these types of alcohols are susceptible to acyl-oxygen fission during hydrolysis. See ref. 2, p. 760.

Hydrolysis of methylvinylcarbinyl acetal in dilute aqueous sulfuric acid yielded methylvinylcarbinol as the only alcoholic product. Substantial amounts of crotyl alcohol should have formed had the methylvinylcarbonium ion served as a reaction intermediate.<sup>10</sup> On hydrolysis in a dilute sulfuric acid solution in aqueous dioxane the levorotatory acetal prepared from (-)- $\alpha$ -phenylethyl alcohol produced alcohol with optical properties identical with those of the material used in synthesis of the acetal. None of the racemization which would attend a carbonium ion path was observed.

When phenylvinylcarbinyl acetal was hydrolyzed by long exposure to a solution of sulfuric acid in aqueous dioxane, the product contained considerable quantities of cinnamyl alcohol. Some or all of this alcohol must have derived from isomerization of phenylvinylcarbinol in the acid medium<sup>11</sup> after its formation as a product of hydrolysis. The composition of the immediate alcoholic hydrolysis product was established through a comparative study of the kinetics of hydrolysis of the acetal and of isomerization of phenylvinylcarbinol in 78% aqueous dioxane solutions of the same acid concentrations. Analysis of samples of the reaction mixtures for phenylvinylcarbinol and cinnamyl alcohol content was accomplished by a procedure which required hydrogenation of the alcohol mixtures. The saturated alcohols were converted to their *p*-nitrobenzoates which were separated by chromatographic methods and weighed. In analyzing the resultant data the entirely reasonable<sup>4,11</sup> assumptions were made that the hydrolysis of the acetal and the isomerization of phenylvinylcarbinol follow rate laws (2) and (3), respectively

$$-d(\text{acetal})/dt = d(\text{alcohol})/2dt = k_1(\text{acetal})(\text{H}^+) \quad (2)$$

$$-d(\text{PhVCOH})/dt = k_2(\text{PhVCOH})(\text{H}^+) \quad (3)$$

Then if phenylvinylcarbinol is the only immediate alcoholic hydrolysis product of the acetal, and cinnamyl alcohol is formed by subsequent isomerization, the concentration of phenylvinylcarbinol at any time *t* in the mixture of alcohols produced during the hydrolysis is given by equation (4)

$$(\text{PhVCOH}) = 2k_1(A^0)(e^{-k_1(\text{H}^+)t} - e^{-k_2(\text{H}^+)t})/(k_2 - k_1) \quad (4)$$

The term (*A*<sup>0</sup>) represents the initial acetal concentration. Values of  $k_1(\text{H}^+) = 0.0246 \text{ min.}^{-1}$  and  $k_2(\text{H}^+) = 1.73 \times 10^{-4} \text{ min.}^{-1}$  were obtained from the hydrolysis and isomerization runs which are summarized in Tables I and II. Table I shows the phenylvinylcarbinol and cinnamyl alcohol concentrations at various times during the hydrolysis run as determined experimentally and as calculated from the observed rate constants by means of equations (2) and (4). The agreement between observed and calculated values is very good.

This result can probably be regarded as satisfactory evidence that the phenylvinylcarbonium ion is not an intermediate in the hydrolysis. Several displacement reactions of cinnamyl halides in hydroxylic solvents, which very likely proceed through formation of cinnamyl-phenylvinylcarbonium ion, in all cases yield mixtures of allylic isomers.<sup>12</sup>

(10) W. G. Young and L. J. Andrews, *THIS JOURNAL*, **66**, 421 (1944).

(11) E. A. Braude, E. R. H. Jones and E. S. Stern, *J. Chem. Soc.*, 396 (1946).

(12) J. Meisenheimer and J. Link, *Ann.*, **479**, 211 (1930).

TABLE I

HYDROLYSIS OF PHENYLVINYL-CARBINYL ACETAL IN 78% AQUEOUS DIOXANE (25°)<sup>a</sup>

Time, min.	Phenylvinylcarbinol, mmole		Cinnamyl alcohol, mmole	
	Obsd.	Calcd.	Obsd.	Calcd.
30	0.274	0.258	0.0000	0.0000
65	.407	.392	.0014	.0018
90	.417	.436	.0046	.0042
170	.476	.477	.0091	.0098
375	.460	.468	.0249	.0239
780	.423	.436	.0586	.0578

<sup>a</sup> The solution was 0.304 *N* in sulfuric acid. The total volume of the original solution was 75 ml. The initial acetal concentration was 0.2465 mmole/5 ml. Reported values for phenylvinylcarbinol and cinnamyl alcohol are given in terms of the number of millimoles contained in a 5-ml. sample of the solution.

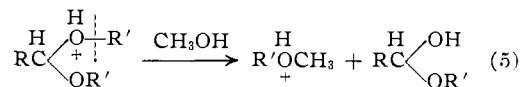
TABLE II

ISOMERIZATION OF PHENYLVINYL-CARBINOL TO CINNAMYL ALCOHOL IN 78% AQUEOUS DIOXANE (25°)<sup>a</sup>

Time, min.	Cinnamyl alcohol, g.	Phenylvinylcarbinol, g.	Recovery of alcohols, %
60	0.0009	0.0864	97.5
180	.0030	.0847	97.8
480	.0074	.0786	96.0
720	.0109	.0760	97.2
1500	.0197	.0683	98.2

<sup>a</sup> The solution was 0.304 *N* in sulfuric acid. The initial solution (75 ml.) contained 1.344 g. of phenylvinylcarbinol. The analyses reported at various times refer to the amounts of alcohols contained in 5-ml. samples of the reaction mixture.

The remote possibility (already rejected for simpler systems<sup>4,7</sup>) that these hydrolyses may have occurred through bimolecular attack of water at the R' groups of the acetal was investigated. This would result in inversion at the carbinol carbon of R'. The configuration at the asymmetric centers of the dextrorotatory acetal derived from (+)- $\alpha$ -phenylethyl alcohol relative to that of its hydrolysis product was established through a study of the acid-catalyzed methanolysis of the acetal. The reaction product was substantially pure (+)- $\alpha$ -phenylethyl alcohol of essentially the same optical purity as the starting alcohol. Had the acetal been subjected to S<sub>N</sub>2 attack by methanol at the R' groups,  $\alpha$ -phenylethyl methyl ether should have formed rather than the alcohol (equation 5 demonstrates the first O-R' cleavage for such a reaction).



It therefore follows that acetal and alcohol which have the same sign of rotation also have the same configuration. Thus hydrolysis of this acetal cannot have occurred by any path requiring O-R' bond ruptures. A trace of  $\alpha$ -phenylethyl methyl ether formed during methanolysis of the acetal was very likely produced by solvolysis of the alcohol product.

### Experimental

**Methylvinylcarbinyl Acetal.**—Twenty grams (0.45 mole) of ice-cold freshly distilled acetaldehyde was added to an equally cold slurry of 20 g. of anhydrous calcium chloride in 32 g. (0.45 mole) of methylvinylcarbinol.<sup>13</sup> One drop of

(13) Prepared from acrolein and methylmagnesium iodide by the method of L. Claisen and E. Tietze, *Ber.*, **59**, 2344 (1926).

saturated ethanolic hydrogen chloride was added, and the mixture was allowed to stand at room temperature for three days in a stoppered flask. The mixture was then filtered, and the solid residue was washed with a small amount of ether. The filtrate and washings were distilled in the presence of 0.25 g. of sodium carbonate. A cut of 35 g. of material, which boiled from 112–148°, was fractionated through a spinning band column to yield 30 g. (79% theory) of methylvinylcarbinyl acetal of b.p. 161.5° (762 mm.),  $n_D^{20}$  1.4192,  $d_4^{25}$  0.8455.

*Anal.* Calcd. for  $C_{10}H_{18}O_2$ : C, 70.52; H, 10.66. Found: C, 70.46; H, 10.72.

**Proof of Structure of Methylvinylcarbinyl Acetal.**—The acetal did not give a positive Tollens test but gave a precipitate of acetaldehyde 2,4-dinitrophenylhydrazone when warmed with a dilute solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The m.p. of the derivative (after purification by chromatographic techniques) and mixed m.p. with an authentic sample was 167–168°.

A mixture of 8.7 g. (0.051 mole) of the acetal in 100 ml. of anhydrous ether and 50 mg. of platinum oxide catalyst was shaken for one hour on a Parr low pressure apparatus at an initial hydrogen pressure of 25 lb./sq. in. After filtration of the catalyst and removal of the solvent, the crude product was fractionated on the spinning band column. A total of 8.0 g. (90% yield) of reduced acetal was collected, b.p. 171.5 (764 mm.),  $n_D^{20}$  1.4024. These physical constants agreed well with those of an authentic sample of *sec*-butyl acetal<sup>7</sup> (b.p. 171–171.5°,  $n_D^{20}$  1.4023) prepared from *sec*-butyl alcohol by the procedure used in preparation of the unsaturated acetal.

Six grams (0.034 mole) of the reduced acetal was stirred for 24 hours at 40° with 50 ml. of 0.1 *N* sulfuric acid. The resultant solution was diluted with 150 ml. of water saturated with sodium chloride and adjusted to alkalinity with sodium carbonate. This solution was continuously extracted with ether for 48 hours. The dried extract was fractionated on a concentric tube column with *n*-hexyl alcohol added to the boiler to assure complete recovery of low boiling product. A total of 4.8 g. (94% yield) of *sec*-butyl alcohol of b.p. 99.5–99.8° (762 mm.), and  $n_D^{20}$  1.3949 was recovered. The 3,5-dinitrobenzoate of this alcohol melted at 75.0–75.6°.

**Hydrolysis of Methylvinylcarbinyl Acetal.**—Hydrolysis of 5.6 g. (0.033 mole) of methylvinylcarbinyl acetal and fractionation of the products was accomplished by exactly the same procedures as were applied in the hydrolysis of *sec*-butyl acetal. A total of 4.4 g. (92% yield) of methylvinylcarbinol was collected at 96–97° (762 mm.). After this cut was taken, the head temperature of the column rose to the boiling point of *n*-hexyl alcohol before further distillate was collected. No *crot*yl alcohol, b.p. 121°, was obtained. The refractive index,  $n_D^{20}$  1.4125, and melting point of the 3,5-dinitrobenzoate, 54°, were in close agreement with values reported previously.<sup>10</sup>

**The Resolution of  $\alpha$ -Phenylethyl Alcohol.**—Eastman Kodak  $\alpha$ -phenylethyl alcohol was resolved by essentially the procedure reported previously,<sup>14,15</sup> which is based on separation of the *d*- and *l*-hydrogen phthalate esters as their brucine salts. The methyl acetate used in recrystallization of these salts was fractionated after refluxing with acetyl chloride. With 1–2% added water the purified solvent could be used to recrystallize the salt with maximum efficiency. The ( $-$ ) $\alpha$ -phenylethyl alcohol thus obtained showed  $[\alpha]_D^{20}$  –43.33° corresponding to an optical purity of 97.2% as based on the data of Downer and Kenyon.<sup>14</sup> The dextrorotatory alcohol showed  $[\alpha]_D^{20}$  +38.69° corresponding to an optical purity of 86.8%.

**$\alpha$ -Phenylethyl Acetal.**—A sample of this acetal was prepared from 72 g. (0.59 mole) of inactive alcohol, 25 g. (0.57 mole) of acetaldehyde and 20 g. of anhydrous calcium chloride by exactly the procedure used in preparing methylvinylcarbinyl acetal. Vacuum distillation of the crude product gave 46 g. (58% yield) of almost colorless  $\alpha$ -phenylethyl acetal, b.p. 152–153° (5.5 mm.). This material gave a negative Tollens test but on warming with acidified 2,4-dinitrophenylhydrazine precipitated acetaldehyde 2,4-dinitrophenylhydrazone.

An analytical specimen of the acetal, obtained by fractionation of a sample on the spinning band column, had the

following properties: b.p. 152.2° (4.6 mm.),  $n_D^{20}$  1.5210,  $d_4^{25}$  1.0062.

*Anal.* Calcd. for  $C_{15}H_{22}O_2$ : C, 79.96; H, 8.20. Found: C, 80.15; H, 8.28.

Samples of the acetal prepared from ( $-$ ) and ( $+$ ) $\alpha$ -phenylethyl alcohol had physical properties almost identical with those given above, and their specific rotations were, respectively,  $[\alpha]_D^{20}$  –211.69° and  $[\alpha]_D^{20}$  +190.14°.

**Hydrolysis of ( $-$ ) $\alpha$ -Phenylethyl Acetal.**—A solution of 6 g. (0.022 mole) of the acetal in 30 ml. of 0.3 *N* sulfuric acid in 78% aqueous dioxane was heated at 60° for two hours. The solution was then extracted with ether, and the ether phase was washed with 5% aqueous sodium bicarbonate and dried over magnesium sulfate. After the ether was removed, the crude product was fractionated on the spinning band column to yield 4.4 g. (82% yield) of ( $-$ ) $\alpha$ -phenylethyl alcohol, b.p. 101° (20 mm.),  $n_D^{20}$  1.5205,  $[\alpha]_D^{20}$  –43.25°.

**Methanolysis of ( $+$ ) $\alpha$ -Phenylethyl Acetal.**—A solution of 7.5 g. (0.028 mole) of ( $+$ ) $\alpha$ -phenylethyl acetal,  $[\alpha]_D^{20}$  +190.14°, in 50 ml. of absolute methanol containing one drop of saturated ethanolic hydrogen chloride was refluxed for 20 hours and then neutralized with 0.1 g. of anhydrous sodium carbonate. Two high boiling cuts were collected by fractionation of this material on the spinning band column. The first cut, 0.21 ml. of b.p. 69–70° (19.5 mm.) and  $[\alpha]_D^{20}$  –3.91°, was presumed to be  $\alpha$ -phenylethyl methyl ether. The second cut, 6.2 ml. of b.p. 99–101° and  $[\alpha]_D^{20}$  +38.62°, was ( $+$ ) $\alpha$ -phenylethyl alcohol of essentially the same optical purity as that of the material used in preparation of the acetal.

The following experiments concerning direct methanolysis of ( $-$ ) $\alpha$ -phenylethyl alcohol suggest that the trace of ether formed in the above reaction derived from the reaction of alcohol (produced in the methanolysis of the acetal) rather than directly from the acetal. From a solution of 5.3 g. of ( $-$ ) $\alpha$ -phenylethyl alcohol in 35 ml. of methanol containing one drop of ethanolic hydrogen chloride there was isolated, after four hours of reflux, 0.3 ml. of ( $+$ ) $\alpha$ -phenylethyl methyl ether, b.p. 70° (20 mm.),  $[\alpha]_D^{20}$  +36.76°. A similar mixture, after 20 hours of reflux, provided 0.85 ml. of the ether of b.p. 69–70.5° (19.5 mm.) and  $[\alpha]_D^{20}$  +15.30°. The configuration of ether was predominantly opposite to that of the starting material,<sup>16</sup> but the magnitude of its rotation diminished with reflux time. The rotation of the alcohol recovered from these reactions was essentially the same as that of the starting material.

**Phenylvinylcarbinyl Acetal.**—This was prepared by the same procedure used in the preparation of methylvinylcarbinyl acetal. From 21 g. (0.16 mole) of phenylvinylcarbinol<sup>17</sup> 15 g. (65% yield) of phenylvinylcarbinyl acetal of b.p. 141–142° (1.8 mm.) was obtained. A small sample of this material was fractionated on the spinning band column to provide an analytical sample of b.p. 120° (0.55 mm.),  $n_D^{20}$  1.5364,  $d_4^{25}$  1.0217.

*Anal.* Calcd. for  $C_{20}H_{26}O_2$ : C, 81.60; H, 7.55. Found: C, 81.68; H, 7.58.

**Proof of Structure of Phenylvinylcarbinyl Acetal.**—The acetal gave acetaldehyde 2,4-dinitrophenylhydrazone when treated by the procedure described for other acetals.

A 7.6-g. sample of the acetal was reduced in 100 ml. of anhydrous ether in the presence of 0.08 g. of platinum oxide by shaking for one hour at a hydrogen pressure of 30 lb./sq. in. Fractionation of the products provided 6 g. (78% yield) of 1-phenyl-1-propyl acetal, b.p. 140° (2 mm.).

This material was identical in physical properties with a sample of 1-phenyl-1-propyl acetal prepared from 1-phenyl-1-propanol and acetaldehyde by the general procedure which has been outlined. The acetal (38% yield) so prepared had the following properties: b.p. 129–129.5° (0.75 mm.),  $n_D^{20}$  1.5160,  $d_4^{25}$  1.0026.

*Anal.* Calcd. for  $C_{20}H_{26}O_2$ : C, 80.52; H, 8.78. Found: C, 80.87; H, 8.88.

The 1-phenyl-1-propanol was prepared by catalytic reduction of 15 g. (0.11 mole) of phenylvinylcarbinol over 0.02 g. of platinum oxide by the method used for reduction of methylvinylcarbinyl acetal. The 12 g. (79% yield) of

(16) E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

(17) Prepared by the method of D. I. Dauven and J. Kenyon, *ibid.*, 1697 (1939).

(14) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939).

(15) E. L. Eliel, *This Journal*, **71**, 3976 (1949).

product had properties, b.p. 103° (15 mm.) and  $n_D^{27}$  1.5120, which agreed favorably with those in the literature.<sup>18</sup>

One gram of the material prepared by reduction of the unsaturated acetal was subjected to hydrolysis by procedures subsequently described in the study of the hydrolysis of phenylvinylcarbinyl acetal. Using the techniques of separation of 1-phenyl- and 3-phenyl-1-propanols as their *p*-nitrobenzoate esters, 0.4 g. of 1-phenyl-1-propyl *p*-nitrobenzoate and none of the isomeric ester was isolated from the hydrolysate.

**Hydrolysis of Phenylvinylcarbinyl Acetal.**—A 1.088-g. sample of this acetal was dissolved in 75 ml. of 0.304 *N* sulfuric acid in 78% aqueous dioxane. Dry nitrogen gas was bubbled through the solution (which was held at 25°) to sweep out acetaldehyde as it formed in order to minimize chances of back reaction. Five-ml. aliquots of the reaction mixture were removed periodically and were quenched in 25 ml. of 5% aqueous sodium carbonate. The carbinol was extracted from these solutions with ether. The dried ether extracts were subjected to hydrogenation over 0.01 g. of platinum oxide at a pressure of 25 lb./sq. in. for 45 minutes. The ether was then removed *in vacuo*, and the residue was treated with 0.3 g. of *p*-nitrobenzoyl chloride in 5 ml. of anhydrous pyridine. After 24 hours this mixture was extracted with four 50-ml. portions of ether. These combined extracts were washed with 10% aqueous sodium carbonate, dried and evaporated under reduced pressure. The residue was dissolved in a total of 8 ml. of Skellysolve B. The solution was applied to a chromatographic column packed with the fluorescent mixture described by White and Dryden,<sup>19</sup> which consisted of silicic acid-diatomaceous filter aid (2-1) impregnated with rhodamine 6 G. The column was developed with a 5% solution of ether in Skellysolve B. Under fluorescent light separation of two dark bands was observed almost immediately. These were collected separately by elution into weighed containers. After these samples were evaporated, the residual yellow oils were re-

frigerated to produce crystallization. In some cases a single seed crystal of the appropriate ester was added. Crystals from the lower band melted from 55–57° and gave no depression when mixed with authentic samples of 1-phenyl-1-propyl *p*-nitrobenzoate.<sup>20</sup> The products from the upper band melted from 45.5–47° and gave no depression with 3-phenyl-1-propyl *p*-nitrobenzoate.<sup>20</sup> In theory analysis of a 5-ml. aliquot on completion of hydrolysis should have provided a total of  $4.95 \times 10^{-4}$  mole of mixed *p*-nitrobenzoates. From the aliquot taken at 780 min. (Table I) a total of  $4.82 \times 10^{-4}$  mole of *p*-nitrobenzoates was recovered. Chromatographic separation of known mixtures of varying composition of the two *p*-nitrobenzoates was always accomplished with better than 99% over-all recovery.

Authentic samples of 3-phenyl-1-propanol required for these experiments were prepared in 91% yield by reduction of cinnamyl alcohol by the procedures used in the reduction of phenylvinylcarbinol. The properties of the product, b.p. 103–5° (6 mm.),  $n_D^{20}$  1.5349, were in agreement with those reported previously.<sup>21</sup>

**The Response of Phenylvinylcarbinol to Procedures Used in Following the Hydrolysis of its Acetal.**—A solution of 1.344 g. of phenylvinylcarbinol in 75 ml. of 0.304 *N* sulfuric acid in 78% aqueous dioxane was maintained at 25°. Five-ml. aliquots of this solution were removed periodically and were subjected to reduction, esterification and chromatographic procedures as applied in the study of the hydrolysis of phenylvinylcarbinyl acetal. The results of these analyses on samples taken at various times are summarized in Table II.

**Acknowledgment.**—The authors are indebted to Professor E. P. Painter for many helpful suggestions concerning this research and to Professor R. E. Kepner and Mr. Robert Ikeda for help with the chromatographic separations.

(20) L. F. King, *THIS JOURNAL*, **61**, 2386 (1939).

(21) (a) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 242 (1924); (b) J. W. Brühl, *Ann.*, **200**, 191 (1879).

DAVIS, CALIFORNIA

(18) (a) R. C. Huston and T. E. Friedmann, *THIS JOURNAL*, **40**, 785 (1918); (b) J. F. Norris and F. Cortese, *ibid.*, **49**, 2645 (1927).

(19) J. W. White, Jr., and E. C. Dryden, *Anal. Chem.*, **20**, 853 (1948).

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY, HARVARD UNIVERSITY]

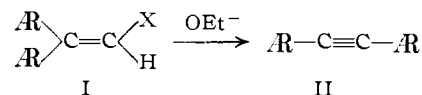
## Stereochemistry of the Rearrangement Involving Migration between Multiply-bonded Carbons

BY AKSEL A. BOTHNER-BY

RECEIVED DECEMBER 22, 1954

*cis*- and *trans*-1-*p*-bromophenyl-1-phenyl-2-bromoethylene-1-<sup>14</sup>C have been prepared and converted by means of potassium *t*-butoxide in *t*-butyl alcohol to labeled 4-bromotolans. The measured radioactivities of the benzoic and *p*-bromobenzoic acids obtained by oxidation of the tolans indicated that the *cis* (bromine and *p*-bromophenyl *cis*) isomer rearranged with 88% migration of the phenyl group while the *trans* isomer rearranged with 92% migration of the *p*-bromophenyl group. Possible mechanisms and implications are discussed.

**Introduction.**—More than sixty years ago it was demonstrated by Fritsch,<sup>1</sup> Buttenberg<sup>2</sup> and Wiechell<sup>3</sup> that the treatment of 1,1-diaryl-2-haloethylenes (I) with sodium ethoxide at 180–200° resulted in a reaction involving elimination and rearrangement to yield substituted tolans (II). Apparently related rearrangements were reported by Tiffeneau<sup>4</sup> (the conversion of 1-bromo-2-phenylpropene to 1-phenylpropyne with molten potassium hydroxide) and more recently by Newman and Kutner<sup>5</sup> (the formation of tolan from 5,5-diphenyl-3-nitroso-2-oxazolidones by alkaline hydrolysis). Potassium amide in liquid ammonia is a particularly suitable



reagent for bringing about the Fritsch–Buttenberg–Wiechell (FBW) rearrangement according to Coleman, *et al.*,<sup>6</sup> who were able by its use to obtain consistently high yields in short reaction times. The rearrangement presents several unusual features, in particular the migration of an aryl group between multiply-bonded carbons.

A striking parallel exists between this rearrangement and the Beckmann rearrangement which is now generally believed to occur by migration of a group between multiply-bonded carbon and nitro-

(1) P. Fritsch, *Ann.*, **279**, 319 (1894).

(2) W. P. Buttenberg, *ibid.*, **279**, 327 (1894).

(3) H. Wiechell, *ibid.*, **279**, 337 (1894).

(4) M. M. Tiffeneau, *Compt. rend.*, **135**, 1374 (1902).

(5) M. S. Newman and A. Kutner, *THIS JOURNAL*, **73**, 4199 (1951).

(6) G. H. Coleman and R. D. Maxwell, *ibid.*, **66**, 132 (1934); G. H. Coleman, W. H. Holst and R. D. Maxwell, *ibid.*, **58**, 2310 (1936).