palladium–charcoal catalyst[14] and six drops of quinoline-S regulator.[15] Hydrogen was passed in slowly with vigorous stirring for 8 to 12 hours at the reflux temperature of the ether At the end of the reaction period, the catalyst was removed by filtration and the filtrate distilled. The fraction boiling at 40–53° was removed and an excess of water (about 18 g., 1 mole) added. The ether was distilled off. The residue consisted largely of a mixture of 1,1-dihydroperfluorobutanol and perfluorobutyraldehydrol from which the aldehyde was recovered upon treatment with sulfuric acid in the manner described above; yield about 6.3 g. (31.8%).

The course of the reaction cannot be followed, as is customary, by the evolution of hydrogen chloride. The latter forms with the aldehyde and ether a distillable molecular complex or ternary azeotrope having the composition corresponding approximately to the formula $C_3F_7CHO \cdot C_2H_5OC_2H_5 \cdot HCl$, b.p. 52–52.5° (737 mm.), n^{25}D 1.3303. *Anal.* Calcd. for $C_8H_{12}O_2ClF_7$: Cl, 11.45. Found: Cl, 10.1.

The distillable complex can also be synthesized by direct addition of hydrogen chloride to an ether solution of perfluorobutyraldehyde.

By very careful addition of a small amount of water it is possible to isolate the free aldehyde from the complex, but the conversion to the aldehydrol is recommended as being more satisfactory and giving a higher over-all yield of aldehyde.

Perfluorobutyraldehyde by the Rosenmund Reduction (Low Pressure Reaction).—In a dry "citrate" pressure bottle were placed 23 g. (0.1 mole) of perfluorobutyryl chloride,[1] 1 g. of palladium–charcoal catalyst[14] and four drops of quinoline-S regulator.[15] The bottle was clamped into a Parr low pressure hydrogenation apparatus[16] and the bottle was "popped" twice (50 p.s.i. hydrogen pressure applied, the bottle opened) to remove the air from the bottle. Hydrogen was then run into the bottle to 50 p.s.i. and the container shaken at room temperature for one week. The pressure drop was about 8 pounds.

The contents of the bottle were placed in a still and the major portion distilling at 28–32° (740 mm.) removed. To this fraction water was added with cooling. The crystalline aldehydrol was recovered by filtration and dried in air; yield 6.87 g. (35%). The aldehyde was obtained by dehydration with concentrated sulfuric acid as described earlier.

Perfluoroacetaldehyde by the Rosenmund Reduction.—In a dry "citrate" pressure bottle was placed 42 g. (0.2 mole) of perfluoroacetic anhydride, 6 g. of diethyl ether saturated with hydrogen chloride, equivalent to 1% Cl^- based on the weight of anhydride used,[17] 2.4 g. of palladium–charcoal catalyst,[14] and 4–6 drops of quinoline-S regulator.[15] The bottle was clamped into a Parr low pressure hydrogenation apparatus[16] and without "popping" the bottle, 50 p.s.i. hydrogen pressure was applied and the container shaken at room temperature until the pressure dropped 12 p. s. i., or until the pressure no longer decreased. The pressure was released and the contents of the bottle were transferred to the pot of a semi-micro vacuum type still, the vacuum outlet attached to a Dry Ice–acetone cooled trap and the liquid portion distilled at atmospheric pressure. A portion of the trifluoroacetaldehyde present collected in the cold trap. The fraction boiling 36–68° (740 mm.) was redistilled in a similar still and a further amount of the aldehyde collected in the cold trap; yield 1.05 g. (5%), b.p. −19° (746 mm.). The fraction distilling at 50–55° (740 mm.) contains 1,1-dihydroperfluoroethyl perfluoroacetate ($CF_3COOCH_2CF_3$), (5 g., 12%, b.p. 55–56° (741 mm.), n^{20}D 1.2772, d^{20}_4 1.464) which lends support to Swarts'[3] claim of obtaining the same compound by the catalytic hydrogenation of perfluoroacetic anhydride. From it he prepared 1,1-dihydroperfluoroethanol by hydrolysis.

Acknowledgments.—We are indebted to B. W. Nippoldt, H. E. Freier and D. G. Weiblen and the Clark Microanalytical Laboratory for the analyses reported in this paper; and to Minnesota Mining & Manufacturing Co. for permission to publish this paper.[18]

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(14) Catalyst may be obtained from the Wilkins–Anderson Company, 111 N. Canal Street, Chicago, Illinois.

(15) R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York. N. Y., 1948, p. 368; E. B. Hershberg and J. Carson, *Org. Syntheses*, **21**, 84 (1941).

(16) Parr Catalytic Hydrogenation Apparatus, Model C. A., Parr Instrument Company, Moline, Illinois.

(17) C. Mannich and A. H. Nadelman, *Ber.*, **63B**, 796 (1930), state that under these conditions anhydrides are converted to the acid chloride, a reaction presumed to occur here also.

(18) Since the original filing date of this paper, U. S. Patents 2,568,500 covering the perfluoroaldehydes and aldehydrols, and 2,568,501 covering the alkylidene diesters have been issued to the authors and assigned to Minnesota Mining and Manufacturing Company.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

Migration Ratios in the Rearrangement of 2,2-Diarylethanols[1]

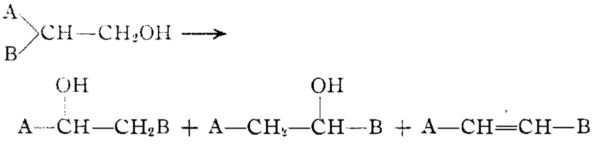
BY JOHN G. BURR, JR., AND LEON S. CIERESZKO[2]

RECEIVED JUNE 7, 1952

The migration ratios with reference to phenyl of eight substituted phenyl groups have been determined by the acid-catalyzed rearrangement of the corresponding 2,2-diarylethanol-1-C^{14}. The values were obtained by oxidation of the stilbene resulting from the rearrangement, and by radiochemical assay of the most easily isolated oxidation product, which in the above cases was a phthalic acid or a substituted benzoic acid. This method of obtaining migration ratios is characterized by lack of stereochemical complications, simplicity of system, easy availability of starting materials, operation on a semi-micro scale, and precision in the determination of the ratios. The meaning of the values here reported is discussed in relation to other values of migration ratios, in terms of Hammett's σ-values, and with reference to the concept of neighboring group participation.

Introduction

One of the simplest possible systems available for investigating the relative migrations of aryl or alkyl groups may be represented as



$$\begin{array}{c}A\\B\end{array}\!\!>CH-CH_2OH \longrightarrow$$

$$A-\underset{\displaystyle}{\overset{OH}{\overset{|}{C}}}H-CH_2B + A-CH_2-\overset{OH}{\overset{|}{C}}H-B + A-CH{=}CH-B$$

Such systems consist only of the two groups, A and B, capable of migration; a two-carbon chain offering the opportunity of rearrangement; and the grouping, –OH, which offers a reactive site where a rearrangement reaction may be initiated with rea-

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(1) This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory. Presented in part at the Milwaukee Meeting of the American Chemical Society, March 30–April 3, 1952.

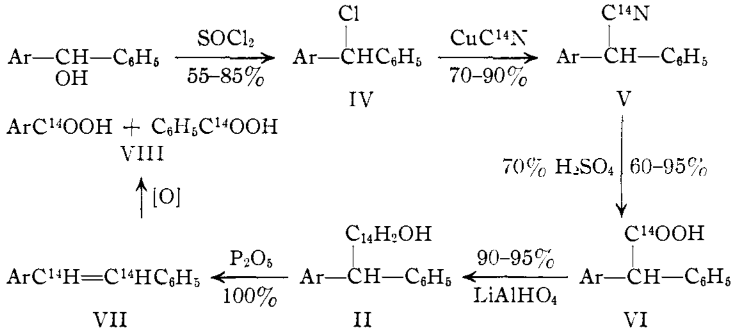
(2) Member of the Research Participation program sponsored jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute of Nuclear Studies; permanent address: University of Oklahoma, Norman, Oklahoma.

gents of known functions. A subsequent paper[3] reports work in a system where –OH has been replaced by $-NH_2$.

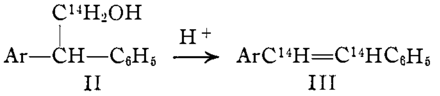
Such systems as these are normally not practical for investigation since the rearrangement products,

$A\text{–}CH{=}CH\text{–}B$, $A\text{–}CH_2\text{–}\overset{\overset{OH}{|}}{C}H\text{–}B$ or $A\text{–}\overset{\overset{OH}{|}}{C}H_2\text{–}CH\text{–}B$, are indistinguishable or difficult to separate quantitatively.

However, by labeling one or the other of the two carbon atoms in the chain with isotopic carbon, the study of such systems as I becomes not only practical but unusually simple from the experimental point of view. Since these systems are free from stereochemical complications, the unambiguous data available from them are of considerable theoretical importance. Moreover, they offer a good opportunity for study under well-controlled conditions with a variety of reagents. For these reasons, we have undertaken at this Laboratory to study several such systems. Preliminary reports on the first two of these studies are made in this and the subsequent paper.[3]



The acid-catalyzed rearrangement of carbon-14 labeled diarylethanols (II) has been the first type



$$\underset{\text{II}}{Ar\text{—}\overset{\overset{C^{14}H_2OH}{|}}{C}H\text{—}C_6H_5} \xrightarrow{H^+} \underset{\text{III}}{ArC^{14}H{=}C^{14}HC_6H_5}$$

of system investigated. The data obtained from eight examples of the rearrangement are reported in Table I. The results on two others, α-naphthyl *versus* phenyl and β-naphthyl *versus* phenyl are reported elsewhere[4] since they were of interest in another problem.

TABLE I

REARRANGEMENTS OF $Ar\text{—}\overset{\overset{C^{14}H_2OH}{|}}{C}H\text{—}C_6H_5$

Ar	Migration of Ar, %	Migration ratio, Ar/C_6H_5
p-Xenyl	57.2	1.34
m-Tolyl	61.3	1.58
p-(2-Propyl)-phenyl	64.5	1.82
3,4-Dimethylphenyl	65.6	1.91
p-Tolyl	66.4 ± 0.95	1.98
p-Ethylphenyl	68.6	2.18
p-(*t*-Butyl)-phenyl	76.3	3.22
p-Methoxyphenyl	95.5	21.2

The general method of synthesis of the labeled diarylethanol is outlined in the flowsheet.

The various substituted diarylacetonitriles were prepared by the reaction of substituted benzhydryl chlorides with cuprous cyanide at a temperature of 200–240° and with a reaction time of one to two hours.[5] This procedure has been employed in the preparation of the eight nitriles reported here with reproducible yields of 70–90%. In the case of *p*-methoxybenzhydryl chloride, the yield was very poor if the reaction temperature exceeded 200°, but good yields were obtained at 180–200°. The procedure is particularly well adapted for the use of $CuC^{14}N$.

Hydrolysis of the nitriles (V) to the acids (VI) could be accomplished either by heating with alcoholic alkali or by the use of boiling 70% sulfuric acid. Generally sulfuric acid gave a better yield and a cleaner product; however, in the case of 2-phenyl-2-(*p*-anisyl)-acetonitrile only a prolonged alkaline hydrolysis was successful.

Reduction of the acids of the carbinols was accomplished in every case with lithium aluminum hydride in ether solution, followed by hydrolysis of the excess reagent with ethyl acetate and just sufficient dilute sodium hydroxide to produce a dry, granular precipitate of inorganic hydroxides which was easily filtered. The rearrangement of the carbinols (II) was carried out by mixing them with a slurry of phosphorus pentoxide in xylene or benzene and bringing this to the boiling point for about 15 minutes. The data obtained by these processes are summarized in Table II.

The stilbenes obtained in the rearrangement were purified by crystallization, and oxidized to an easily isolable acid. The acids obtained, and the conditions employed are summarized in Table III.

Four representative sets of radiochemical data are summarized in Table IV.

Wherever a conveniently purifiable intermediate in the reaction sequences was encountered it was assayed for carbon-14. This was done principally to establish a reliable base level of activity from which to calculate the migration ratio and to eliminate the possibility of a shift in activity level owing to isotope selectivity in incomplete reactions.[6]

Table IV includes activity data on several diarylethylamine hydrochlorides, since for these particular examples they formed part of the base level of activity. These amines were obtained by reduction of the nitriles and were used for a study of the amine–nitrous acid rearrangement. This is reported in a subsequent paper.[3]

The compounds occurring in the other examples (see Table I) were all prepared from the same batch

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(3) L. S. Ciereszko and J. G. Burr, THIS JOURNAL, **74**, 5431 (1952).

(4) C. J. Collins, J. G. Burr, Jr., *et al.*, *ibid.*, in press. Our interest in this problem is derived from the work of Collins and his collaborators. *Cf.* Collins, *et al.*, *ibid.*, **73**, 5176 (1951).

(5) While this work was in progress, Budde and Potempa reported the preparation of diphenylacetonitrile from the reaction of benzhydryl bromide and cuprous cyanide at 125° (*ibid.*, **74**, 248 (1952)). However, the benzhydryl chlorides are more easily and economically prepared than the bromides.

(6) *Cf.* G. A. Ropp and O. K. Neville, *Nucleonics*, **9**, 22 (1951), for a general review of the isotope effect.

TABLE II

Ar	Chloride M.p., °C.	Chloride Yield, %	Nitrile M.p., °C.	Nitrile Yield, %	Acid M.p., °C.	Acid Yield, %	Carbinol M.p., °C.	Carbinol Yield, %	Stilbene M.p., °C.	Stilbene Yield,^{ff} %
p-Tolyl	Oil	84	60-61^a	64	110–112^b	89	43–44^c	93	120^d	100
p-Ethylphenyl	Oil	..	Oil	90	78^e	65	Oil^f	95	82^g	100
p-(2-Propyl)-phenyl	Oil	..	Oil	86	Oil^h	54	Oil	92	80^i	100
p-(*t*-Butyl)-phenyl	Oil	..	98^j	76	139^k	57	82^l	100	96^m	100
3,4-Dimethylphenyl	Oil	79	54^n	70	124^o	70	Oil^p	90	78^q	100
m-Tolyl	B.p. 136^r	..	26^s	80	122^t	93	Oil^u	92	49–50^v	100
p-Xenyl	62^w	72	131-132^x	70	143-144^y	88	100–101^z	88	222^{aa}	100
p-Methoxyphenyl	61^{bb}	55	130^{cc}	71	96^{dd}	68	Oil	93	135^{ee}	100

[a] Lit. 61°, Michael and Jean Pretre, *Ber.*, **25**, 1676 (1892). [b] Lit. 115°, McKenzie and Widdows, *J. Chem. Soc.*, **107**, 713 (1915). [c] Lit. 45–46°, Reinart and Amagat, *Compt. rend.*, **179**, 901 (1924). [d] Lit. 120°, Anschütz, *Ber.*, **18**, 1946 (1888). [e] Calcd. for $C_{16}H_{16}O_2$: C, 79.2; H, 6.64. Found: C, 79.2; H, 6.84. [f] α-Naphthylurethan, m.p. 92°. Calcd. for $C_{27}H_{25}O_2N$: N, 3.54. Found: N, 3.43. [g] Calcd. for $C_{16}H_{16}$: C, 92.2; H, 7.74. Found: C, 92.1; H, 7.85. [h] Amide, m.p. 97. Calcd. for $C_{17}H_{19}ON$: N, 5.52. Found: N, 5.62. Anilide, m.p. 211°. Calcd. for $C_{23}H_{23}ON$: N, 4.25. Found: N, 4.16. [i] Calcd. for $C_{17}H_{18}$: C, 90.8; H, 8.18. Found: C, 91.0; H, 8.09. Dibromide, m.p. 228°. Calcd. for $C_{17}H_{18}Br_2$: Br, 41.6. Found: Br, 41.7. [j] Calcd. for $C_{18}H_{19}N$: N, 5.61. Found: N, 5.61. [k] Calcd. for $C_{18}H_2O_2$: C, 80.6; H, 7.53. Found: C, 80.5; H, 7.64. [l] Calcd. for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 84.8.; H, 8.83. [m] Calcd. for $C_{16}H_{20}$: C, 91.5; H, 8.54. Found: C, 91.54; H, 8.54. Dibromide, m.p. 230°. Calcd. for $C_{18}H_{21}Br_2$: Br, 40.4. Found: Br, 40.6. [n] Calcd. for $C_{16}H_{11}N$: N, 6.35. Found: N, 6.36. [o] Calcd. for $C_{16}H_{16}O_2$: C, 80.1; H, 6.70. Found: C, 80.0; H, 6.61. [p] α-Naphthylurethan, m.p. 149°. Calcd. for $C_{27}H_{25}O_2N$: N, 3.54. Found: N, 3.54. [q] Calcd. for $C_{16}H_{16}$: C, 92.2; H, 7.74. Found: C, 92.1; H, 7.66. [r] Pressure of b.p., 1 mm.; $n^{25}D$ 1.5850; $d^{25}{}_4$ 1.109; *MR*D, calcd. 65.14, found, 65.48. [s] $n^{25}D$ 1.5760. [t] Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.24. Found: C, 79.9; H, 6.36. [u] α-Naphthylurethan, m.p. 118°. Calcd. for $C_{26}H_{23}O_2N$: N, 3.67. Found: N, 3.80. [v] Lit. 48°, Bergmann and Schapiro, *J. Org. Chem.*, **12**, 57 (1947); dibromide 178°, lit. 176°; *ibid.* [w] Lit. 62.5°, Wittig and Petri, *Ann.*, **513**, 26 (1934). [x] Lit. 130–131°, Wittig and Petri, ref. *w*. [y] Lit. 141–142°, Blicke and Grier, THIS JOURNAL, **65**, 1725 (1943). [z] Calcd. for $C_{20}H_{18}O$: C, 87.5; H, 6.57. Found: C, 87.4; H, 6.60. [aa] Lit. 221°, Bergmann and Weymann, *J. Org. Chem.*, 9, 415 (1944). [bb] Calcd. for $C_{14}H_{13}OCl$: Cl, 15.2. Found: Cl, 15.3. [cc] Calcd. for $C_{15}H_{13}ON$: N, 6.27. Found: N, 6.30. [dd] Lit. 100° Poincet, *Compt. rend.*, **148**, 419 (1909). [ee] Lit. 135–136°, Van Duin, *Rec. trav. chim.*, **45**, 347 (1926). [ff] Although the yields of purified stilbenes usually were less than 100%, the residual material was very high boiling and was presumably polymeric stilbene.

TABLE III

$ArCH{=}CHC_6H_5$ Ar	Oxidation conditions	Isolated oxidation product, acids
p-Xenyl	Neutral $KMnO_4$ in aqueous acetone	*p*-Phenylbenzoic
m-Tolyl	Alkaline $KMnO_4$ in water	Isophthalic
p-(2-Propyl)-phenyl	Alkaline $KMnO_4$ in water	Terephthalic
3,4-Dimethylphenyl	Alkaline $KMnO_4$ in water	Trimellitic
p-Tolyl	Alkaline $KMnO_4$ in water	Terephthalic
p-Ethylphenyl	Alkaline KMnO in water	Terephthalic
p-(*t*-Butyl)-phenyl	CrO_3 in HOAc	*t*-Butylbenzoic
p-Methoxyphenyl	Neutral $KMnO_4$ in aqueous acetone	Hydroxybenzoic^a

[a] The oxidation products were benzoic and anisic acids. The anisic acid was cleaved as described in the Experimental section.

TABLE IV

The Numerals in the Table Refer to C^{14} Activities in μc./Mmole

Derivative	*p*-Tolyl	*m*-Tolyl	*p*-Xenyl	*p*-Anisyl
Diarylacetic acid (VI)	4.40	4.08	4.32	4.04
Diarylethylamine hydrochloride	4.45	4.06	4.23	(4.00)^a
Stilbene (VII)	4.31	4.10	...	4.10
Average of above three	4.39	4.08	4.25	4.05
Oxidation product (see Table III)	2.84	2.50	2.43	3.87
Migration of substituted phenyl, %	64.7	61.3	57.2	95.5

[a] This value is for the *p*-anisyl phenylacetonitrile.

of cuprous cyanide-C^{14}, and the base level of activity used for the calculation of the migration ratios in these cases was the average of 29 determinations, taken on 13 intermediates from six different series of rearrangements. Its value was 1.69 ± 0.05 μc. of C^{14}/mmole. This is also the base level of activity for reference in Table V below. The value of the migration ratio for 2-phenyl-2-(*p*-tolyl)-ethanol-1-C^{14} listed in Table I is the average value obtained from six separate rearrangements and its value is 66.4 ± 0.95% (average deviation).

In carrying out the rearrangements as mentioned above, it occurred to us that the rearrangement might be complete at some temperature below the boiling point of the xylene used in most cases. Since the temperature of the rearrangement was thus indeterminant and possibly significant, a series of rearrangements were carried out under a wide variety of experimental conditions on one of the cases, 2-phenyl-2-(*p*-tolyl)-ethanol-1-C^{14}. The results are summarized in Table V. It is evident that the migration ratio of *p*-tolyl *versus* phenyl is relatively insensitive to these variations in the conditions of rearrangement.

TABLE V

Reagent	Solvent	*T*, °C.	Terephthalic acid μc. of C^{14}/mmole
P_2O_5	Xylene	90	1.15
P_2O_5	Xylene	139	1.14
P_2O_5	None	200	1.13
$KHSO_4$	None	200	1.10
$ZnCl_2$	None	200	1.13

Since the irreversibility of this rearrangement should be demonstrated, a sample of stilbene (obtained during the work shown in Table V) was resubmitted to phosphorus pentoxide in benzene. However, the only product was a polymer which could not be degraded. Another sample of this stilbene was converted to the dibromide. The stilbene regenerated from this dibromide by treatment with sodium iodide in acetone upon oxidation gave terephthalic acid with a carbon-14 content of 1.13 μc./mmole, essentially unchanged.

The starting materials for these investigations are easily prepared and the reactions involved are simple and proceed in good yield. Reliable data can be obtained from quite small scale operations—on a 1–2-g. scale. In several cases as little as 100 mg. of stilbene from the rearrangement gave sufficient oxidation product for repeated assay. Finally, owing to the simplicity, precision and speed of carbon-14 determinations by wet combustion and ionization chamber-vibrating reed counting (a complete determination including final calculations can be carried out in 20 minutes), the determination of migration ratios can be made with great facility and a precision of about 2–3%. By employing several known refinements in technique, this precision could be made much greater.

Experimental[7]

Since each one of these series of compounds was carried through a similar set of reactions under closely similar conditions, and since the pertinent experimental data are summarized in Table I, only the experimental details of the 2-phenyl-2-(*p*-anisyl)-ethanol-1-C^{14} series are reported. In addition, the oxidation of *t*-butylstilbene is discussed since this proved to be difficult.

***p*-Methoxybenzhydryl Chloride.**—The reduction of 106 g. of *p*-methoxybenzophenone with zinc dust and alkali in alcohol solution gave a non-crystalline benzhydrol. This sirup was dried and then refluxed in benzene solution with 40 ml. of thionyl chloride. The volatile solvents and excess thionyl chloride were removed by distillation and the dark residual sirup distilled under high vacuum. The light green distillate was redistilled to give, in several fractions, 58 g. (55%) of a colorless liquid which immediately solidified and was recrystallized to give white needles melting at 61°; Norris and Banta[8] report this as red oil.

Anal. Calcd. for $C_{14}H_{13}OCl$: Cl, 15.2. Found: Cl, 15.3.

2-Phenyl-2-(*p*-anisyl)-acetonitrile-1-C^{14}.—An intimate mixture of 8.3 g. of the above chloride and 3.2 g. of cuprous cyanide-C^{14} (prepared[9] by the interaction of cupric sulfate, sodium bisulfite and sodium cyanide-C^{14} and dried in a 110° oven) was prepared, and the flask containing it was immersed in an oil-bath preheated to 180°. After one hour (during which the bath temperature rose to 190°), the flask was removed and partially cooled. The still fluid product was extracted with chloroform, and the filtered chloroform solution concentrated and then diluted with hexane. The first crop of nitrile (2.8 g., m.p. 130°) crystallized out on cooling. By reworking the filtrate, an additional 2.0 g. could be obtained; total yield 4.8 g. (71%). Recrystallization did not raise the melting point above 130°; assay: 4.00, 4.00 μc. of C^{14}/mmole.

2-Phenyl-2-(*p*-anisyl)-acetic-1-C^{14} Acid.—Hydrolysis of the nitrile in boiling 70% sulfuric acid for from one to six hours produced only neutral gums. However, when 2.85 g. of the nitrile was refluxed with a solution of 15 g. of potassium hydroxide in a mixture of 15 ml. of water and 50 ml. of ethanol for two days, the acidic product was 3.08 g. of a light brown oil. Repeated extraction of this with boiling hexane and recovery of the acid from the hexane gave a white crystalline acid, m.p. 96° (2.37 g., 68%); assay: 4.04 μc. of C^{14}/mmole.

2-Phenyl-2-(*p*-anisyl)-ethanol-1-C^{14}.—The acid (2.00 g.) was refluxed for one hour with 2.0 g. of lithium aluminum hydride in about 75 ml. of ether. The excess hydride was destroyed by cautous addition of ethyl acetate, and the hydrolysis completed with 10% sodium hydroxide, added until the precipitate just coagulated and settled. Filtration and evaporation of the dried filtrate gave 1.75 g. (93%) of a colorless oil.

***p*-Methoxystilbene-α,α'-C^{14}.**—The non-crystalline carbinol obtained above was added to a suspension of phosphorus pentoxide in 25 ml. of xylene, and this mixture heated to boiling. After 15 minutes, the solution was cooled, the xylene decanted and the flask rinsed with ether. The filtered solution was evaporated (after boiling with Nuchar), and the pale yellow crystalline residue crystallized from hexane to give 0.65 g. of the stilbene as colorless prisms melting at 135°. More could be obtained from the filtrate; assay: 4.09, 4.11 μc. of C^{14}/mmole.

Oxidation of *p*-Methoxystilbene-α,α'-C^{14}.—A sample of the stilbene (0.50 g.) was refluxed for 15 minutes with a solution of 3 g. of potassium permanganate in a mixture of 45 ml. of acetone and 30 ml. of water. The precipitated manganese dioxide was filtered off, and the colorless filtrate concentrated in an air blast to remove acetone. It was then acidified and ether-extracted. Evaporation of the ether extract gave 0.60 g. of a mixture of benzoic and anisic acids. This mixture was dissolved in 30 ml. of benzene and the solution refluxed 1.5 hours with 2 g. of aluminum bromide. Hydrolysis with concentrated hydrochloric acid, ether-extraction, and evaporation of the dried ether extract gave 0.50 g. of demethylated acid mixture. Extraction of this with carbon disulfide gave a residue of crude *p*-hydroxybenzoic acid (0.15 g.) which after crystallization from dilute alcohol (Norite) formed a white crystalline powder melting at 213–214°; assay: 3.90, 3.92, 3.80 μc. of C^{14}/mmole. A second recrystallization did not change the C^{14} value.

Oxidation of *p*-(*t*-Butyl)-stilbene-α,α'-C^{14}.—On the small scale employed (0.5–1.0 g.) this material proved extremely resistant to the desired type of oxidation. Oxidations with neutral permanganate, gave an inseparable mixture of benzoic and *t*-butylbenzoic acids. Alkaline permanganate oxidations gave either a mixture of benzoic acid and *t*-butylbenzoic acid or no isolable oxidation products. Finally, it was discovered that refluxing the stilbene with chromium trioxide in acetic acid solution for 20 minutes gave a sample of pure *t*-butylbenzoic acid, m.p. 165° after two crystallizations from dilute ethanol.

Discussion

The vast amount of data which has been obtained on the subject of the relative migration tendencies of substituted aryl groups in rearrangement reactions[10] present a very confusing picture. In some of the reactions studied, notably the work of Bachmann on the symmetrical pinacol rearrangement,[11] these migrations appear to form a consistent relationship with each other. However, when other reactions and types of compounds are studied, the consistency observed among the symmetrical pinacols does not appear. For example, the following values have been reported for the migration ratio of *p*-xenyl to phenyl: 11.5,[11] 1.18,[12] 1.88,[13] 1.87,[14] 3.75,[14] 1.34,[15] 1.00,[3] 1.08,[16] 13.3,[17] in various cases.

It is undoubtedly true that some of this variation in migration ratios is caused by factors such as a change in the carbonium ion intermediate (compare the ratios observed in unsymmetrical pinacols), the possibility of *cis–trans* isomerism[16] or by the failure to obtain constant stereochemical form and

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(7) Melting points were taken either upon a calibrated Fisher-Johns block or upon a Kofler Heizbank. C-14 assays were accomplished by a wet combustion of the compounds, and ionization chamber counting of the evolved carbon dioxide on a vibrating reed electrometer. Microanalyses for carbon, hydrogen, nitrogen and halogen were done by Dr. H. W. Galbraith, Knoxville, Tennessee.

(8) J. F. Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).

(9) H. J. Barber, *J. Chem. Soc.*, 79 (1943).

(10) For excellent reviews on the state of this subject see G. W. Wheland "Advanced Organic Chemistry," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 12; and also H. Gilman, "Organic Chemistry," 2nd Ed., Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1943, Chapter 12. These reviews contain good summaries of the early literature in this field.

(11) W. E. Bachmann and J. W. Ferguson, THIS JOURNAL, **56**, 2081 (1934) .

(12) W. E. Bachmann and H. R. Steinberger, *ibid.*, **56**, 170 (1934).

(13) W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952).

(14) H. H. Hatt, A. Pilgrim and E. F. M. Stephenson, *J. Chem. Soc.*, **478** (1941).

(15) This work.

(16) P. A. S. Smith and J. P. Horwitz, THIS JOURNAL, **72**, 3718 (1950).

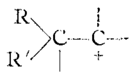
(17) R. N. Lewis and J. R. Wright, *ibid.*, **74**, 1257 (1952).

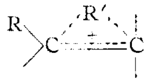
purity in the pinacols or amino alcohols concerned.[18] However, these factors cannot account for all of the observed variation since some of these data are drawn from reaction systems and substances where stereochemistry is unimportant (for example, the work reported here and in the subsequent paper[3]). It appears consistent to conclude that migration ratios are related to factors which are dependent upon the reaction system itself. Such factors would include the nature of the reaction, the type of reactants, and the reaction conditions.

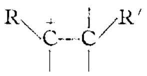
The migration ratios reported here do not give a straight line when plotted as logarithms against Hammett's σ-values.[19] The ratios obtained by Bachmann[11] in the rearrangement of symmetrical pinacols, similarly show no linear correlation[13] with the Hammett σ-values. The lack of such a relationship both in the data presented here, and in Bachmann's data, seems reasonable since these rearrangements resemble in many respects aromatic substitution,[20] and there does not appear to be much evidence showing that the rates of aromatic substitution follow a linear Hammett relationship. Since it does not seem probable that migration ratios in an acid-catalyzed rearrangement should be expected to follow a Hammett plot, the recent observation by McEwen[13] of a set of ratios which do follow such a plot is difficult to explain. However, the mechanism for the reaction of diarylethylenes with hydrogen azide does not appear to have been definitely established.[21]

Since neither the existing data on migration ratios nor the concept of a linear Hammett relationship seem able to explain migration selectivity, theoretical grounds which will allow consistent prediction of migration ratios can probably be achieved only if this problem can be explained in terms of some understood and measurable aspect of the system.

Acid-catalyzed rearrangements such as discussed in this paper have long been considered to proceed through transition states including bridged carbonium ions such as X.[22] A rearrangement proceeding through such a transition state would necessarily require participation by the aryl groups, R and R', in the formation of the transition state. Recent work has given strong evidence for the ability of aryl groups to participate in the formation of carbonium ion transition states.[23]


XI


X


XI

Since it thus seems probable that the aryl groups present in our diarylethanols do assist in the formation of the carbonium ion intermediate, it is reasonable to expect that substituted aryl groups will thus participate to different degrees, and to conclude that the relative migrations of these aryl groups may be a function of their ability to participate. In this way, it would be possible to explain migration selectivity in terms of the known and measurable concept of neighboring group participation. Since the extent of neighboring group participation can be determined for a number of different systems, a dependence of migration selectivity upon participation should enable the precise and consistent prediction of migration ratios in these same systems.

The verification of such a relationship does not fall within the scope of the data presented in this paper, since the migration ratios reported here were obtained under conditions where simultaneous observation of participation was impossible. However, since the verification of such a relationship is important, experiments are under way in this Laboratory designed to secure simultaneously data on the migration ratios and degrees of participation of several aryl groups.

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(18) For examples illustrating the importance of this factor in compounds which occur both in racemic and *meso* forms, see Gaertner, *J. Org. Chem.*, **15**, 1006 (1950); Curtin and Pollak, THIS JOURNAL, **73**, 992 (1951); **72**, 961 (1950). The existence of this factor was originally observed by W. E. Bachmann and Shankland, *ibid.*, **51**, 306 (1929); and also by Bergmann and Schuchardt, *Ann.*, **487**, 234 (1931).

(19) L. P. Hammett, "Physical Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 198.

(20) G. W. Wheland, ref. **10**, p. 517.

(21) W. E. McEwen, M. Gilliland and B. I. Sparr, THIS JOURNAL, **72**, 3212 (1950).

(22) Early speculations concerning the existence of bridged ions as intermediates in molecular rearrangements are well summarized by S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952); and S. Winstein, *et al.*, *ibid.*, **74**, 1114 (1952) Recent advances in this field, have been summarized by P. D. Bartlett (Organic Symposium, June 1951, Denver, Col.); and J. D. Roberts (120th Meeting of the American Chemical Society, New York City, September, 1951). Important recent papers include: (1) S. Winstein, *et al.*, THIS JOURNAL, **70**, 838 (1948), which gave evidence for the existence of bridged ions in the *i*-sterol rearrangement; and (2) D. J. Cram, *et al.*, *ibid.*, **71**, 3683 (1949), which gave evidence for the direct formation of phenonium ions. Many points in these earlier papers have been elaborated in papers by Cram, *et al.*, *ibid.*, **74**, 2129 (1952) *et seq.*; and the recent papers by Winstein and his group mentioned above.

(23) This evidence is found in many of the papers listed in the previous reference.[22] The articles by Cram deal first and most exclusively with the evidence for the existence of phenonium ions (*i.e.*, transition states such as X); but a great deal of evidence is also found in the papers by Winstein and his group including especially S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952). Of course, the evidence presented in these papers deals with solvolytic rearrangements in homogeneous systems, but it seems reasonable to extend the concept to the type of heterogeneous acid catalysis described in this paper.