The question of neighboring group participation in the Wagner rearrangement of 9-fluorenylcarbinols, and the steric effect owing to substitution at the 1-position of these carbinols will be the subject of future reports.

Acknowledgment.—The authors are indebted to Dr. J. D. Roberts and to Dr. W. M. Lauer for many valuable suggestions during the course of this work.

OAK RIDGE, TENNESSEE

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

Studies in the Wagner Rearrangement.[1-3] IV. The Steric Effect of an Ortho Methyl Group

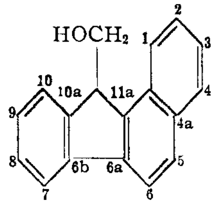
BY BEN M. BENJAMIN[4] AND CLAIR J. COLLINS

RECEIVED JUNE 16, 1952

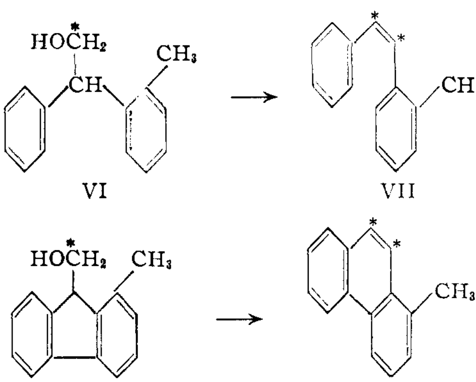
2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI) and 1-methyl-9-fluorenyl-(carbinol-C^{14}) (XIV) have been converted by the Wagner rearrangement to labeled *o*-methylstilbene (VII) and labeled 1-methylphenanthrene (XV), respectively. Chemical degradation of the *o*-methylstilbene (VII) indicated that the phenyl group of VI had migrated in preference to the *o*-tolyl group in the ratio 55:45. Degradation of the labeled 1-methylphenanthrene (XV) showed that the phenylene and *o*-tolylene fragments of XIV had migrated in the ratio 50:50. These results show that although the methyl group of VI exerts a small steric effect during rearrangement, the methyl group in 1-methyl-9-fluorenylcarbinol exerts a negligible over-all effect on the dehydration–rearrangement of this latter compound.

Introduction

In prior papers[1] syntheses of carbon-labeled phenanthrene, benz[a]anthracene and chrysene through the dehydration–rearrangements of substituted 9-fluorenylcarbinols have been reported. While the carbon-14 was nearly equally distributed between the two labeled positions of benz[a]anthracene, it was distributed between the 5- and 6-positions of chrysene in the ratio of 76:24. It was suggested[1c] that the carbon and hydrogen in the 1-position of 11H-benzo[a]fluorene-11-methanol exert little if any steric influence during the rearrangement of this carbinol. It was of interest therefore to study the Wagner rearrangement of 1-methyl-9-fluorenylcarbinol (XIV), since from molecular models of XIV there is indicated very little hindrance between the methyl and carbinol groups of this compound. In 2-phenyl-2-(*o*-tolyl)-ethanol (VI) however, the methyl group should be free to exert its steric hindrance to *o*-tolyl migration by limiting rotation about the bond connecting the tolyl group with the tertiary carbon, and thus limiting the probability of orientations favorable to *o*-tolyl group migration. While it is in fact probable that there is a steric interaction between the *o*-tolyl and phenyl groups of compound VI owing to the methyl residue, it seems unlikely that the mobility of the phenyl group is affected to exactly the same degree as that of the *o*-tolyl group.



11H-Benzol[a]fluorene-11-methanol



VI VII

XIV XV

If these postulates are true, then the phenyl group of carbinol VI should migrate with higher frequency than the phenylene group of carbinol XIV during the Wagner rearrangements of these compounds. A comparison of the carbon-14 distributions in the products VII and XV, obtained from the labeled carbinols VI and XIV, respectively, should therefore permit a qualitative test of our hypothesis.

Rearrangement of 2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI).—2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI) was prepared by the general procedure of Burr and Ciereszko.[5] The synthesis of this carbinol, its rearrangement to labeled *o*-methylstilbene (VII), and the degradative procedure used to locate the radioactivity in the latter compound are shown in the reaction series IV → X inclusive. Each labeled position is indicated by the asterisk (*). Radioactivities are shown under the appropriate structures and are expressed as microcuries of carbon-14 per millimole (μc./mmole). From the millimolar ra-

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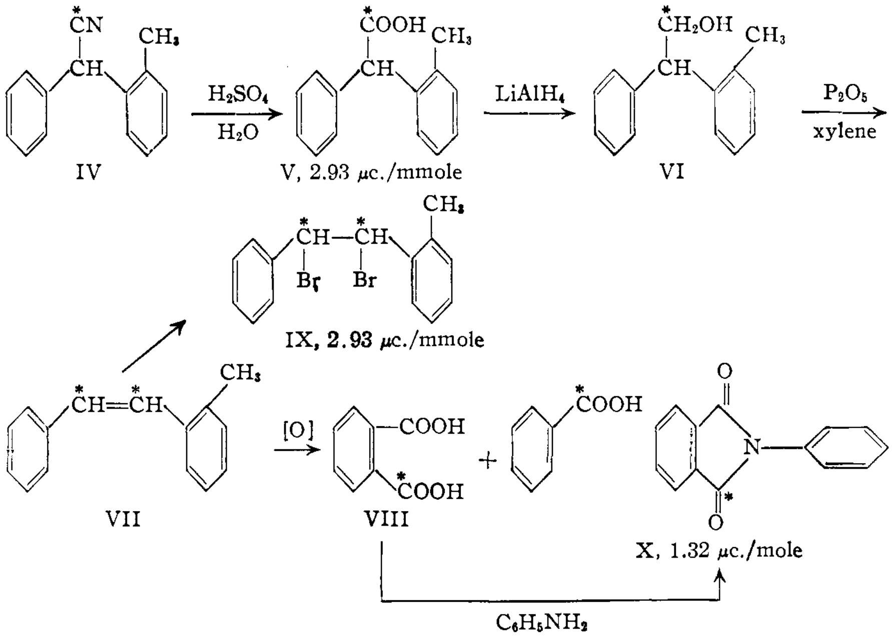
[1] Previous papers: (a) I, C. J. Collins, THIS JOURNAL, **70**, 2418 (1948); (b) II, C. J. Collins, J. G. Burr and D. N. Hess, *ibid.*, **73**, 5176 (1951); (c) III, C. J. Collins, D. N. Hess, R. H. Mayor, G. M. Toffel and A. R. Jones, *ibid.*, **75**, 397 (1953).

[2] This paper is based upon work performed under Contract Number W-7405-eng 26, for the Atomic Energy Commission at the Oak Ridge National Laboratory.

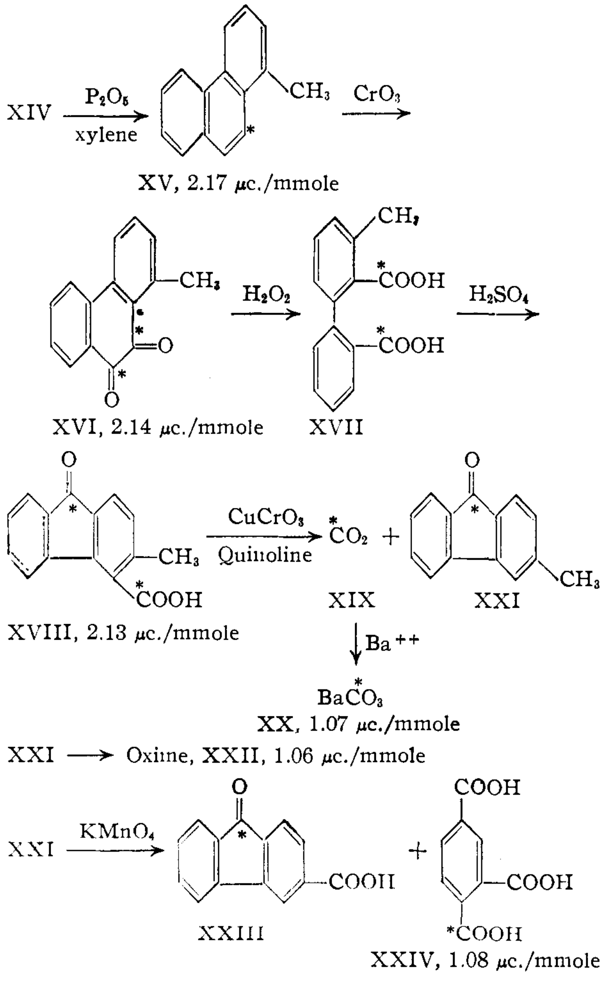
[3] From the Ph.D. Thesis of Ben M. Benjamin.

[4] Graduate Fellow from the University of Florida, Gainesville, Florida. Fellowship sponsored jointly by the Oak Ridge Institute of Nuclear Studies and the Oak Ridge National Laboratory.

[5] Drs. J. G. Burr, Jr., and L. Ciereszko, in this Laboratory, have prepared a series of unsymmetrically meta- and para-substituted 2,2-diphenylethanols.



dioactivities of compounds V (2.93 µc.), IX (2.93 µc.) and X (1.32 µc.), it is apparent that the phenyl group of 2-phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI) has migrated in preference to the *o*-tolyl group during the dehydration–rearrangement in the ratio of 55:45.



Rearrangement of 1-Methyl-9-fluorenyl-(carbinol-C^{14}) (XIV).—1-Methyl-9-fluorenyl-(carbinol-C^{14}) (XIV) was prepared and converted to 1-methylphenanthrene-9,10-C_1^{14} (XV) by methods analogous to those previously described.[1] The degradative procedure used to locate the radioactivity in structure XV is shown in the reaction series XV → XXIV. Although attempts to purify 3-methylfluorene-9-C^{14}-one (XXI) were unsuccessful, the oxime XXII was easily prepared and purified. When the ketone XXI was oxidized with permanganate, both benzene-1,2,4-tricarboxylic acid (XXIV) and fluorenone-3-carboxylic acid (XXIII) were isolated. Radioactivities are shown under the appropriate structures as microcuries per millimole (µc./mmole) of compound. The values expressed for compounds XXII (1.06 µc.) and XXIV (1.08 µc.) represent the carbon-14 present in the 9-position of the 1-methylphenanthrene (XV) while that given (1.07 µc.) for barium carbonate-C^{14} (XX) represents the carbon-14 present in the 10-position of XV. The ratio of the radioactivities of positions 9 and 10 of the 1-methylphenanthrene is therefore 50:50, and the phenylene and *o*-tolylene fragments of carbinol XIV must have migrated with equal frequency during the rearrangement of the latter compound.

Experimental[6,7,8]

2-Phenyl-2-(*o*-tolyl)-acetonitrile-1-C^{14} (IV).—2-Methylbenzophenone (I) was reduced[9] to 2-methylbenzohydrol (II).[10] It was converted with thionyl chloride to 2-methylbenzohydryl chloride (III).[11] A mixture of 25.76 g. of III and 7.19 g. of cuprous cyanide-C^{14} (prepared by the method of Barber)[12] was heated on an oil-bath for an hour at 250°. The nitrile IV was isolated in 83% yield (13.6 g.) based on cuprous cyanide-C^{14}; b.p. 109–111° at 0.06–0.08 mm.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.9; H, 6.32. Found: C, 86.8; H, 6.20.

2-Phenyl-2-(*o*-tolyl)-acetic-1-C^{14} Acid (V).—This acid (3.5 g.) was obtained in almost quantitative yield when the nitrile IV (3.4 g.) was hydrolyzed in 70% sulfuric acid by heating the vigorously stirred mixture under a reflux condenser for two hours. The acid was crystallized six times from cyclohexane; m.p. 96–97.6°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.24. Found: C, 79.2; H, 6.02; microcuries of carbon-14 per millimole of V, 2.93.

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(6) Melting points are uncorrected.

(7) Carbon and hydrogen analyses were performed by Dr. H. W. Galbraith, Knoxville, Tennessee.

(8) Radioactivity assays were performed as described previously[1] using the Van Slyke wet combustion method, and ion chambers in conjunction with the vibrating-reed dynamic condenser electrometer.

(9) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 90.

(10) A. F. Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, **41**, 1116 (1910); *C. A.*, **4**, 1488 (1910).

(11) J. F. Norris and J. T. Blake, THIS JOURNAL, **50**, 1808 (1928).

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

2-Phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI).—The acid V (2 g.) was reduced with excess lithium aluminum hydride. The carbinol VI (1.5 g.) was isolated in 80% yield. It was crystallized five times from cyclohexane; m.p. 58.5–59°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.60. Found: C, 85.3; H, 7.46.

2-Methylstilbene-α,α′-C_1^{14} (VII) and 2-Methylstilbene-α,α′-C_1^{14} Dibromide (IX).—The carbinol VI (1.5 g.) was dissolved in xylene. Phosphorus pentoxide was added and the mixture was heated under a reflux condenser for one-half hour. The oily 2-methylstilbene (VII) was isolated in quantitative yield (1.5 g.). A portion was heated with bromine in carbon tetrachloride solution for one hour. The dibromide was crystallized from isopropyl alcohol; m.p. 160° (lit.[13] 159°).

Anal. Microcuries of carbon-14 per millimole of IX, 2.93.

Oxidation of 2-Methylstilbene-α,α′-C_1^{14}.—The oxidation was effected in two steps. An acetic acid solution of 1.2 g. of VII was heated under a reflux condenser with 4 ml. of 40% peracetic acid. All solvents were removed with a current of air. To the solid residue was added 50 ml. of water and 4 g. of potassium permanganate. The mixture was heated with boiling for an hour. Excess permanganate was decomposed with ethanol. The manganese dioxide was removed by filtration and was washed with dilute base. The basic solution was extracted with ether. The aqueous solution was acidified and was extracted continuously with ether for six hours. When the ether was evaporated, a crystalline residue remained. It was washed with chloroform and crystallized from acetone–chloroform mixture; yield 70.5 mg. The phthalic acid was converted to phthalanil (X) by heating it with aniline. The phthalanil was crystallized from ethanol; m.p. 206–207°.

Anal. Microcuries of carbon-14 per millimole of X, 1.32.

1-Methyl-9-fluorenecarboxylic-C^{14} Acid (XII).—This acid was prepared from 1-methylfluorene[14] (XI) triphenylmethylsodium and carbon-C^{14} dioxide. The procedure used has been described before.[1] The acid was crystallized three times from benzene; m.p. 222.5–223.0°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.40. Found: C, 79.7; H, 5.36.

Methyl 1-Methyl-9-fluorenecarboxylate-C^{14} (XIII).—The ester (1.1 g.) was prepared from 1.076 g. of the acid XII and excess diazomethane in ether solution. A pure sample was obtained by crystallization of the ester seven times from cyclohexane; m.p. 95.0–96.5°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.92. Found: C, 80.2; H, 5.57.

1-Methyl-9-fluorene-(methanol-C^{14}) (XIV).—An ether solution of lithium aluminum hydride was added to 0.966 g. of the ester XIII in dry ether. The carbinol was isolated in quantitative yield (0.865 g.) and was crystallized four times from cyclohexane; m.p. 85.5–86.4°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.71. Found: C, 85.9; H, 6.62.

1-Methylphenanthrene-9,10-C_1^{14} (XV).—To a solution of 0.567 g. of the carbinol XIV in 20 ml. of xylene was added 4 g. of phosphorus pentoxide. The mixture was heated under a reflux condenser for one-half hour. The yield (0.531 g.) of crude yellow product, obtained after washing the xylene solution with alkali and concentration of the solution, was quantitative. The material was purified by dissolving it in benzene, passing the benzene solution through a short alumina column, and evaporating the benzene. The solid residue was crystallized twice from ethanol (Norite); m.p. 119.5–120.5°. Pschorr[15] gives m.p. 121°. When this material was mixed with an authentic sample prepared by the Haworth synthesis[16] the melting point was not depressed.

High Level Synthesis of 1-Methylphenanthrene-9,10-C_1^{14} (XV).—The above procedure was used to prepare 5.17 millimoles (75.4% of the theoretical based on carbon-C^{14} dioxide of specific activity 2.85 μc./mmole) of XV. Purification was performed only on the final product, and the intermediate compounds were not isolated. For the degradative procedures 7.16 mg. of the labeled 1-methylphenanthrene so obtained was mixed with 5450 mg. of non-radioactive 1-methylphenanthrene. The diluted compound was crystallized from ethanol and assayed.

Anal. Microcuries of carbon-14 per millimole of diluted XV, 2.17.

1-Methylphenanthrenequinone-9,10-C_1^{14} (XVI).—Potassium dichromate (5 g.) was added to a solution of 1.03 g. of XV in 20 ml. of acetic acid. The mixture was heated under a reflux condenser for five hours. Dilute hydrochloric acid was added and the quinone along with some acetic acid was removed by continuous extraction with ether. When the solvents had been evaporated in a current of air, 0.842 g. (59%) of impure quinone remained. The product was crystallized from acetone; m.p. 196° (lit.[15] 196°).

Anal. Microcuries of carbon-14 per millimole of XVI, 2.14.

3-Methyldiphenyl-2,2′-dicarboxylic-C_1^{14} Acid (XVII).—The acid was obtained as a crude product in 85% yield (267 mg.) by oxidizing 285 mg. of the quinone XVI in 15 ml. of acetic acid with 2 ml. of 30% hydrogen peroxide. The solution was heated under a reflux condenser for two hours and was allowed to stand at room temperature for 12 hours. Acetic acid was removed in a current of air on the steam-bath. The acid residue was taken up in sodium bicarbonate solution and non-acidic material was removed by continuous extraction with ether. The aqueous solution was acidified and the organic acid was removed by continuous extraction with ether. The acid XVII was purified by crystallization from chloroform; m.p. 190–191°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.3; H, 4.72; neut. equiv., 128. Found: C, 70.1; H, 4.72; neut. equiv., 131.

3-Methylfluorene-9-C^{14}-one-4-carboxylic Acid and 3-Methylfluorene-9-one-4-carboxylic-C^{14} Acid[17] (XVIII).—A solution of 106 mg. of XVII in 15 ml. of 96% sulfuric acid was stirred at room temperature with a magnetic bar for 21 hours. The acid was poured onto ice and the yellow solid which separated was extracted with ether. The residue which remained after the ether was evaporated was taken up in sodium bicarbonate solution and the solution was treated with Norite. The yellow solid was precipitated with dilute acid and was removed by filtration. It was crystallized from benzene; m.p. 206°. The yield was 76 mg. (77% of the theoretical).

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.23. Found: C, 75.0; H, 4.29; microcuries of carbon-14 per millimole of XVIII, 2.13.

3-Methylfluorene-9-C^{14}-one (XXI).—Decarboxylation was effected by heating under a reflux condenser 63 mg. of XVIII in 15 ml. of freshly distilled quinoline with 50 mg. of copper chromite catalyst for about 45 minutes. During this time the apparatus was swept continuously with helium. The carbon-C^{14} dioxide XIX was caught in a barium hydroxide trap. The barium carbonate-C^{14} XX was washed with water and then washed twice with acetone, and dried (yield 49.3 mg.).

Anal. Microcuries of carbon-14 per millimole of XX, 1.07.

The quinoline solution was added to dilute hydrochloric acid and this solution was extracted with ether. The ether layer was shaken first with dilute acid, then with dilute base, and the ether was finally evaporated. The orange residue (69 mg.) could not be caused to crystallize. It was converted to the oxime XXII which was crystallized from cyclohexane seven times; m.p. 185°. A mixed melting point with the oxime prepared from an authentic sample of 3-methylfluorene[18] was not depressed.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.4; H, 5.26. Found: C, 80.0; H, 5.38; microcuries of carbon-14 per millimole of XXII, 1.06.

Oxidation of 3-Methylfluorene-9-C^{14}-one.—A portion of the impure fluorenone XXI was oxidized by heating it under a reflux condenser with 230 mg. of potassium permanganate in 40 ml. of water for one hour. Two acids were isolated from the oxidation mixture. The water-insoluble portion was yellow; m.p. 280°. During a non-radioactive preparation

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(13) F. Bergmann and D. Schapiro, *J. Org. Chem.*, **12**, 57 (1947).

(14) N. C. Deno, THIS JOURNAL, **72**, 4057 (1950).

(15) R. Pschorr, *Ber.*, **39**, 3111 (1906).

(16) R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

(17) This substance XVII is a mixture, each labeled species of which contains carbon-14 in only one of the two possible positions.

(18) F. Ullmann and Ed. Mallet, *Ber.*, **31**, 1684 (1898).

this material was identified as fluorenone-3-carboxylic acid (lit.[19] m.p. 286°). A larger quantity (18 mg.) of water-soluble acid XXIV was isolated; m.p. 195–200°. This was identified as trimellitic acid. The m.p. of an analytical sample was 206°.

Anal. Calcd. for $C_9H_6O_6$: C, 51.4; H, 2.86. Found: C, 51.6; H, 2.92; microcuries of carbon-14 per millimole of XXIV, 1.08.

Discussion of Results

The observed carbon-14 distribution in the product VII is good evidence for a steric effect owing to the *o*-methyl group during the dehydration–rearrangement of 2-phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI). The difference from unity of the ratio (55.0 ± 0.5/45.0 ± 0.5 = 1.22 ± 0.01) of phenyl to *o*-tolyl migration is clearly much greater than the error inherent in the radioactivity determinations so that the greater per cent. of phenyl migration is a real and significant value.

The carbon-14 distribution in the product XV indicates that the over-all influence of the methyl group on the dehydration–rearrangement of 1-methyl-9-fluorenylcarbinol (XIV) is negligible, since the phenyl and *o*-tolyl moieties in this carbinol have migrated in the ratio of 50:50. This result is quite unexpected in view of the known electrical effect of a methyl group.[20] If the steric effect of the methyl group in XIV is assumed to be negligible (*vide supra*), then the electrical effect of the methyl group must also be assumed to be negligible. A negligible electrical effect could be explained on the basis of a resonance interaction between the phenyl and *o*-tolyl moieties of XIV through the biphenyl (4a–4b) bond. The only other plausible explanation for the equal migration ratios of the phenyl and *o*-tolyl moieties of XIV would be that the electrical and steric effects of the methyl group almost exactly cancel each other. In the hope that additional data may be gathered which would allow a choice between these two explanations, the dehydration–rearrangement of 3-methyl-9-fluorenyl-(carbinol-C^{14}) is under investigation. It is assumed that the time variable (electromeric) and static (inductive) effects of the methyl groups in this latter compound and in XIV should be nearly identical.

The rearrangement of carbinols VI and XIV may be formulated as proceeding through resonance-stabilized intermediates analogous to those discussed in the preceding paper.[1c,21]

Acknowledgment.—The authors are indebted to Drs. G. B. Butler, W. M. Lauer and J. D. Roberts for many helpful suggestions during the course of this research.

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[19] A. Sieglitz and J. Schalzhes, *ibid.*, **54**, 2070 (1921).

[20] Drs. J. G. Burr and L. S. Ciereszko in this Laboratory have shown that the *p*-tolyl group in 2-phenyl-2-(*p*-tolyl)-ethanol-1-C^{14} migrates in preference to the phenyl group in the ratio of 66:34 when this carbinol is subjected to the conditions of the Wagner rearrangement.

[21] This formulation is similar to that supported by Cram to explain his results in the Wagner–Meerwein rearrangements of isomers of 3-phenyl-2-butanol and similar compounds: D. J. Cram, THIS JOURNAL, **71**, 3863 (1949); D. J. Cram and R. Davis, *ibid.*, **71**, 3871 (1949); D. J. Cram, *ibid.*, **71**, 3875 (1949).

OAK RIDGE, TENNESSEE

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

Studies in the Wagner Rearrangement. V. Further Evidence for a Steric Effect[1,2]

BY CLAIR J. COLLINS, LEON S. CIERESZKO[3] AND JOHN G. BURR, JR.

RECEIVED JUNE 16, 1952

The radioactivity distributions in the products of the dehydration–rearrangement of 2-phenyl-2-(α-naphthyl)-ethanol-1-C^{14} and 2-phenyl-2-(β-naphthyl)-ethanol-1-C^{14} have been determined and the per cent. migrations of the phenyl and naphthyl groups have been calculated for each system. These migration ratios are: α-naphthyl:phenyl = 52:48; β-naphthyl:phenyl = 56:44. The present results are compared with previous work, and are discussed with respect to steric considerations and the presumed carbonium ion intermediates.

Introduction

The Wagner rearrangements of 11H-benzo[b]fluorene-11-methanol-C^{14} (I, 52% β-naphthyl migration, 48% phenyl migration)[4a] and of 11H-benzo[a]fluorene-11-methanol-C^{14} (II, 76% α-naphthyl migration and 24% phenyl migration)[4b] have been reported. For the latter reaction it was suggested that the steric influence of the carbon and hydrogen at the 1-position of II should be either very small or negligible. Next 1-methyl-9-fluorenyl-(carbinol-C^{14}) (V) and 2-phenyl-2-(*o*-tolyl)-ethanol-1-C^{14} (VI) were prepared and subjected to the conditions of the Wagner rearrangement.[2] While the results indicated a steric effect during the rearrangement of VI, the methyl group in V had no apparent over-all influence on the course of the rearrangement of this carbinol, since the ratio of phenyl to *o*-tolyl migration was 50:50. This result was unexpected since, if the methyl group of V exerts no steric effect, the electromeric and inductive effects of this methyl group should enhance the migration tendency of the *o*-tolyl fragment of carbinol V.

In the present paper we report the migration ratios during the Wagner rearrangements of

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[1] This paper is based upon work performed under Contract Number W-7405-eng 26, for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper, B. M. Benjamin and C. J. Collins, THIS JOURNAL, **75**, 402 (1953).

[3] Member of the Research Participation Program jointly sponsored by the Oak Ridge Institute of Nuclear Studies and this Laboratory, September, 1951–February, 1952.

[4] (a) C. J. Collins, J. G. Burr and D. N. Hess, THIS JOURNAL, **73**, 5176 (1951); (b) C. J. Collins, D. N. Hess, R. H. Mayor, G. M. Toffel and A. R. Jones, *ibid.*, **75**, 397 (1953). The migrating groups are connected by a biphenyl-type bond, and thus are not strictly "naphthyl" and "phenyl" groups. In the interest of ease of expression, however, these fragments, as well as other migrating fragments in the 9-fluorenylcarbinol series, will be referred to by these simpler names.