From titration of standard samples of *o*- and *p*-nitrophenol and *o*- and *p*-nitrophenylpiperidine it was discovered that only *p*-nitrophenol consumes the expected four equivalents per mole under the conditions of bromination used. The other three products consumed fewer equivalents, as follows: *o*-nitrophenol, 3.6; *p*-nitrophenylpiperidine, 3.1; *o*-nitrophenylpiperidine, 2.9. It was therefore necessary to apply a correction factor to each titer, taking into account also the ratios in which the two types of product are formed from each substrate. The correction factors used were: *4-Tos*, 4.0/3.9; *2-Tos*, 4.0/3.52; *4-Mes*, 4.0/3.62; *2-Mes*, 4.0/3.33.

Use of these correction factors did not much affect the values of rate coefficients. "Corrected" coefficients were mostly about 10% higher than those computed without use of the correction. The greatest increase (about 25%) was with *2-Mes*. The values in Table II are all "corrected."

A pseudo-first-order rate coefficient was reckoned (graphically) for each run, and converted to a second-order coefficient by dividing by the piperidine concentration. The latter was multiplied by the experimentally determined fractions of C—O and S—O scission to give, respectively, k_C and k_S.

It was determined that the substrates are not brominated under the conditions of the analysis.

Data for a typical run are given in Table III.

Deamination of 1,2,2-Tri(*p*-anisyl)ethylamine-1-C^{14}

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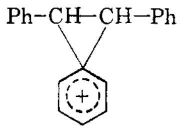
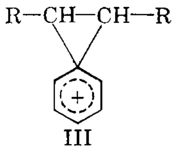
1,2,2-Tri(*p*-anisyl)ethylamine-1-C^{14} (VI, 2.592 mc./mole) was subjected to deamination with nitrous acid, producing 1,2,2-tri(*p*-anisyl)ethanol-1,2-C^{14} (X). Oxidation of the latter to the corresponding ketone, followed by cleavage with alkali afforded di(*p*-anisyl)methane (0.432 mc./mole) and *p*-anisic acid (2.083 mc./mole). These results, indicating a *p*-anisyl migration of only 17% during the deamination, contrast sharply to the 26–28% phenyl migration noted during similar deamination of 1,2,2-triphenylethylamine-1-C^{14}. A rationalization of this observation is offered, involving the suggestion that the cationic charge distribution at the migration terminus is important in determining relative migratory tendencies in 1,2-shifts.

$$\mathrm{Ph_2C_\beta H{-}\overset{\oplus}{C}_\alpha HPh} \rightleftarrows \mathrm{Ph\overset{\oplus}{C}_\beta H{-}C_\alpha HPh_2}$$

I

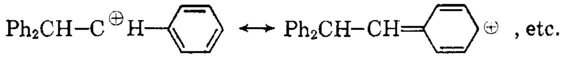


II

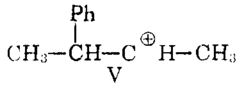


III

In recent years we have studied solvolytic[2] and deamination[3] reactions in the 1,2,2-triphenylethyl system by both radiochemical[2,3] and stereochemical[4] techniques, with the purpose of gaining information as to the type of cationic intermediate (open, classical *vs.* nonclassical, bridged) through which such reactions proceed. All our data, both radiochemical and stereochemical, could be qualitatively and quantitatively interpreted in terms of equilibrating, classical 1,2,2-triphenylethyl carbonium ion intermediates such as I, with bridged phenonium structures such as II being specifically excluded. These conclusions contrasted sharply to those reached by Cram and co-workers[5] in their studies of solvolytic reactions in the 3-phenyl-2-butyl and similar systems and to related deamination reactions,[6,7] wherein convincing evidence was presented for the intervention (partial or complete) of nonclassical phenonium ion intermediates such as III. One possible reason for such mechanistic differences arises from the fact that the open 1,2,2-triphenylethyl carbonium ion may be resonance stabilized as a hybrid (IV) of lower energy than the corresponding bridged ion II. The 3-phenyl-2-butyl carbonium ion (V), on the other hand, has no such effective means of stabilization and presumably is therefore a higher energy species than the corresponding bridged ion III (R = CH_3). In the hope of gaining further insight into questions such as these we have now

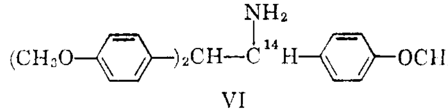


IV



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle Ph}{|}}{C}H{-}\overset{\oplus}{C}H{-}CH_3}$$

V



VI

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[1] The authors are indebted to the National Science Foundation (NSF-G9479) for its generous support of this investigation.

[2] (a) W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953); (b) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955); (c) W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99 (1955).

[3] W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956).

[4] C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959); C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961).

[5] D. J. Cram, *ibid.*, **71**, 3863, 3875 (1949); **47**, 2129, 2137, 2149, 2152, 2159 (1952); D. J. Cram and R. Davis, *ibid.*, **71**, 3871 (1949); D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); F. A. A. Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); D. J. Cram and F. A. A. Elhafez, *ibid.*, **75**, 3189 (1953); D. J. Cram and J. Allinger, *ibid.*, **79**, 2858 (1957).

[6] D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

[7] W. A. Bonner and D. D. Tanner, *ibid.*, **80**, 1447 (1958).

undertaken a study of the nitrous acid deamination of 1,2,2-tri(*p*-anisyl)ethylamine-1-C^{14} (VI), the first substituted analog of the 1,2,2-triphenylethyl system to be investigated.

The question of comparative migratory aptitudes of substituted aryls *vs.* phenyl in 1,2-shifts is one which has received considerable attention.[8] In general, in systems where stereochemical or steric factors or factors involving facilitation of functional group removal are not dominant, the migratory aptitude of a substituted aryl group qualitatively parallels the electron releasing abilities of the substituent.[8a] Several "anomalous" migratory aptitudes in the rearrangements of aldehydes into ketones have recently been clarified,[9] and the principal exceptions to the above generalization, those involving semipinacolic deaminations in the 1-aryl-1,2-diphenyl-2-aminoethanol system, have received adequate rationalization on stereochemical grounds.[10] As a corollary, of all aryl groups *p*-anisyl generally migrates most effectively when pitted against phenyl in 1,2-shifts. Thus in the original studies of Bachmann[11] on the rearrangement of symmetrical pinacoles of the type ArAr′C(OH)C(OH)Ar′Ar, *p*-anisyl migrated about 500 times as readily as did phenyl. In the Wagner-Meerwein rearrangement occurring during dehydration of 2-phenyl-2-(*p*-anisyl)ethanol, 96% of the product was that of *p*-anisyl migration.[12] *p*-Anisyl to phenyl migration ratios between 6 and 100 have been observed in Schmidt rearrangements involving 1,1-diarylethylenes,[13] substituted benzhydrols,[14] and methyldiarylmethyl azides.[15] The predominance of *p*-anisyl over phenyl migration during deamination reactions is again general, but somewhat less spectacular. Thus Curtin and Crew[16] noted a *p*-anisyl/phenyl migration ratio of 1.5 in the deamination of 1-phenyl-1-(*p*-anisyl)-2-aminoethanol, Ciereszko and Burr[17] observed about the same ratio in the deamination of 2-phenyl-2-(*p*-anisyl)ethylamine-1-C^{14} and Roberts[18] found that 2-(*p*-anisyl)ethylamine-1-C^{14} underwent only 1.2–1.9 times as much rearrangement (depending on solvent) on deamination as did 2-phenylethylamine-1-C^{14}. The lower *p*-anisyl/phenyl migration ratios in deamination reactions have been explained[16,17] by the lesser need of anchimeric assistance by the departing $—N_2^+$ group of diazotized amines as compared to the greater anchimeric assist (better furnished by *p*-anisyl than by phenyl) required in solvolytic reactions. The generally observed preference of *p*-anisyl over phenyl migration in *all* systems (except those stereochemically determined[10]) little prepared us for the result which we discovered in the nitrous acid deamination of VI.

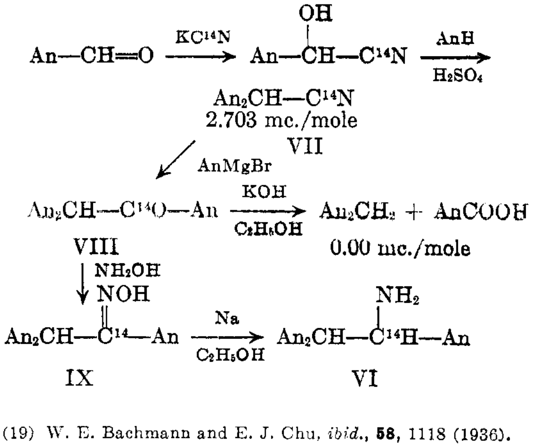
1,2,2-Tri(*p*-anisyl)ethylamine-1-C^{14} (VI) was synthesized from anisaldehyde by the reaction sequence shown in Chart I. A preliminary radioactivity assay (2.703 mc./mole) was conducted on the crystalline di(*p*-anisyl)acetonitrile-C^{14} intermediate (VII). The slightly lower radioactivity assays of the succeeding *p*-anisyl di(*p*-anisyl)methyl ketoxime-C^{14} (IX) (2.627 mc./mole; 2.8% low) as well as that of the final amine VI (2.592 mc./mole; 1.3% low) are in accord, at least, with normal isotope effects in the indicated Grignard and oxime reduction reactions.

In our present system the alkaline degradation[10,19] of *p*-anisyl di(*p*-anisyl)methyl ketone-C^{14} (VIII) appeared more promising than oxidation[2,3] as an analytical tool for determining the extent of label rearrangement. To test this method, phenyl benzhydryl ketone-C^{14} (1.801 mc./mole)[2a] was cleaved with sodium ethylate into benzoic acid (1.802 mc./mole) and diphenylmethane (2,2′,4,4′-tetranitro derivative, 0.0013 mc./mole). The essential absence (0.07%) of radioactivity in the diphenylmethane cleavage product indicated the validity of this degradative procedure. When this degradative technique was applied to the radioactive ketone intermediate VIII in Chart I, the absence of radioactivity in the di(*p*-anisyl)methane product provided a radiochemical structure proof of ketone VIII.

1,2,2-Tri(*p*-anisyl)ethylamine-1-C^{14} (VI), as its

CHART I. THE SYNTHESIS AND RADIOCHEMICAL STRUCTURE PROOF OF 1,2,2-TRI(*p*-ANISYL)ETHYLAMINE-1-C^{14}

(An = *p*-$CH_3O—C_6H_4$—)



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[8] (a) G. Wheland, "Advanced Organic Chemistry," 3rd ed., J. Wiley and Sons, Inc., New York, N. Y., 1960, pp. 573–610; (b) H. Adkins in G. Gilman, "Advanced Organic Chemistry," Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1066–1069; (c) C. J. Collins, *Quart. Rev.*, **14**, 357 (1960).

[9] B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4329 (1956); V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958); L. W. Kendrick, Jr., B. M. Benjamin, and C. J. Collins, *ibid.*, **80**, 4057 (1958); C. J. Collins and N. S. Bowman, *ibid.*, **81**, 3614 (1959).

[10] P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950); D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 992 (1951); D. Y. Curtin, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954).

[11] W. E. Bachmann and F. H. Moser, *J. Am. Chem. Soc.*, **54**, 1124 (1932); W. E. Bachmann and J. W. Ferguson, *ibid.*, **56**, 2081 (1934).

[12] J. G. Burr, Jr., and L. S. Ciereszko, *ibid.*, **74**, 5426 (1952).

[13] W. E. McEwen, M. Gilliland, and B. I. Sparr, *ibid.*, **72**, 3212 (1950).

[14] R. F. Tietz and W. E. McEwen, *ibid.*, **77**, 4007 (1955).

[15] S. N. Ege and K. W. Sherk, *ibid.*, **75**, 354 (1953).

[16] D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

[17] L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952).

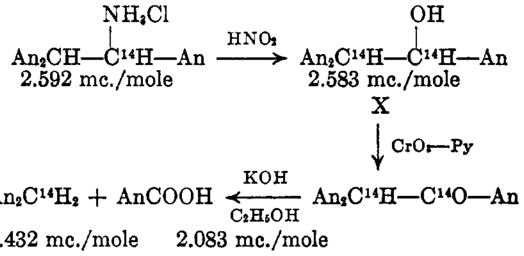
[18] J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953).

[19] W. E. Bachmann and E. J. Chu, *ibid.*, **58**, 1118 (1936).

hydrochloride, was converted in aqueous solution into 1,2,2-tri(*p*-anisyl)ethanol-1,2-C^{14} (X) by the action of nitrous acid (Chart II). The carbinol X was investigated for its label distribution by preliminary oxidation with chromic anhydride–pyridine to labeled *p*-anisyl di(*p*-anisyl)methyl ketone, a process known by analogy to go without rearrangement,[20] followed by alkaline cleavage of the latter ketone. There resulted samples of di(*p*-anisyl)methane having a specific radioactivity of 0.432 mc./mole and of *p*-anisic acid having a specific activity of 2.083 mc./mole. The 2.6% discrepancy in the radiochemical balance of the degradation step in Chart II may be explained by a normal isotope effect of about 0.95, as the anisic acid yield in this step was 63%.[21] The conclusions below are not prejudiced by this minor imbalance.

CHART II. DEAMINATION OF 1,2,2-TRI(*p*-ANISYL)ETHYLAMINE-1-C^{14}

(An = *p*-$CH_3O—C_6H_4—$)



$$An_2CH—\overset{NH_3Cl}{C^{14}H}—An \xrightarrow{HNO_2} An_2C^{14}H—\overset{OH}{C^{14}H}—An$$

$$\text{2.592 mc./mole} \qquad \text{2.583 mc./mole (X)}$$

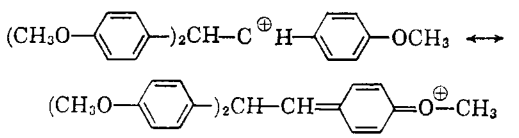
$$\downarrow CrO_3—Py$$

$$An_2C^{14}H_2 + AnCOOH \xleftarrow[C_2H_5OH]{KOH} An_2C^{14}H—C^{14}O—An$$

$$\text{0.432 mc./mole} \qquad \text{2.083 mc./mole}$$

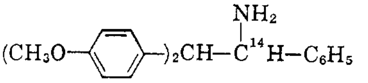
The data in Chart II indicate that the tri(*p*-anisyl)amine VI is deaminated to the corresponding carbinol X with approximately 17% *p*-anisyl migration. The deamination of the corresponding 1,2,2-triphenylethylamine-1-C^{14}, however, is attended by 26–28% phenyl migration.[3,4] The present *p*-*anisyl migration is thus only about 63% as complete as the previously observed phenyl migration.* As outlined above, *p*-anisyl generally migrates markedly more effectively than does phenyl, and a rationalization of our novel result clearly appears required.

Since the deaminations of 1,2,2-triphenylethylamine[3,4] as well as of 1,1-diphenyl-2-amino-1-propanol[22] have been shown to proceed through open rather than bridged carbonium ions, it is safe to assume that the present deamination of VI also occurs through similar classical intermediates. (It should be noted in passing that the sole intervention of a bridged phenonium intermediate would require a 50:50 distribution of label between C-1 and C-2 in the alcohol product X.) If resonance hybrids such as IV stabilize the classical 1,2,2-triphenylethyl carbonium ion, the more favorable hybrid XI must stabilize the 1,2,2-tri(*p*-anisyl)ethyl carbonium ion to an even greater extent. Granting this, our explanation for the unexpectedly low *p*-anisyl migration in the present system is as follows. If the nucleophilicity of the group at the migration origin is of importance in determining migratory tendency, it is reasonable that the electrophilic character of the migration terminus should be similarly important. Thus, while the enhanced nucleophilicity of the *p*-anisyl group makes generally for its greater migratory propensity, the diminished positive character of the migration terminus in XI (as compared with the migration terminus of IV) makes for a lesser tendency toward migration in the present instance. If the latter effect should outweigh the former, as it apparently does in the present case, a diminished tendency toward 1,2-migration should result. We believe this example provides a clear-cut illustration that the cationic charge distribution at the migration terminus dictates relative migration tendencies in 1,2-shifts.[23]

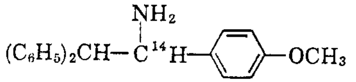


XI

This explanation permits certain predictions with regard to deamination reactions of mixed *p*-anisyl phenyl analogs. If correct, then the deamination of 1-phenyl-2,2-di(*p*-anisyl)ethylamine-1-C^{14} (XII) should proceed with *more* than the 26–28% migration noted for 1,2,2-triphenylethylamine-1-C^{14}, while the deamination of 1-(*p*-anisyl)-2,2-diphenylethylamine-1-C^{14} (XIII) should occur with *less* than the 17% migration observed in the present study. Experiments along these and related lines are currently planned.



XII



XIII

Experimental

Di(*p*-anisyl)acetonitrile-C^{14} (VII).—This was prepared by a procedure essentially similar to that of Sumrell and Goheen.[24] Freshly distilled *p*-anisyldehyde (35 g.) was added to sodium bisulfite (30 g.) in water (100 ml.), and the mixture was stirred vigorously for 1 hr. at 0°, after which the bisulfite complex was filtered and washed with cold water. The complex was then stirred with water (20 ml.) and a solution of potassium cyanide-C^{14} (18.5 g., 10% excess) in water (25 ml.) was added dropwise with stirring. The mixture was stirred for 2.5 hr. at 0° and extracted with

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[20] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 427 (1953).

[21] C. J. Collins, private communication; *cf.*, C. J. Collins and M. H. Lietzke, *ibid.*, **81**, 5379 (1959).

[22] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

[23] See also: L. W. Kendrick, Jr., B. M. Benjamin, and C. J. Collins, *ibid.*, **80**, 4057 (1958); S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

[24] G. Sumrell and G. E. Goheen, *ibid.*, **77**, 3805 (1955).

ether, the extracts being washed with water and dried over magnesium sulfate. Solvent removal *in vacuo* afforded 39.0 g. (93%) of crude *p*-anisyldehyde cyanohydrin. To this was added anisole (39 g.) and the mixture was cooled to 0°, treated slowly with cold 85% sulfuric acid (135 ml.), allowed to stand for 1 hr. and was finally poured into water (1000 ml.). The crude nitrile was filtered, washed, and air-dried. The 42 g. (70%) of crude di(*p*-anisyl)acetonitrile-C^{14} was dissolved in hot glacial acetic acid (200 ml.) and the solution was cooled to room temperature, yielding 36.3 g. of nitrile. The latter was dissolved in chloroform and the solution was washed with saturated sodium bicarbonate, with water, and was dried over potassium carbonate. Solvent removal left 36.2 g. of product which was dissolved in boiling chloroform (200 ml.). The boiling solution was treated with *n*-hexane (200 ml.), cooled to room temperature, and treated with additional *n*-hexane (200 ml.). Chilling to 0° for several hours yielded 35.2 g. (58%) of product having m.p. 156–157° in agreement with the reported value[24] of 156–158.5°. The product had a radioactivity assay[25] of 2.703 mc./mole.

***p*-Anisyl Di(*p*-anisyl)methyl Ketone-C^{14} (VIII).**—This substance was prepared according to the procedure of Sumrell and Goheen.[24] From 44.0 g. of di(*p*-anisyl)acetonitrile-C^{14} was obtained 21.1 g. (26%) of *p*-anisyl di(*p*-anisyl) methyl ketone-C^{14} anisolate, m.p. 70–74°, in fair agreement with the recorded[24] m.p. 77–79°. The complex was employed without further purification, being converted to the free ketone by heating at 90° (0.1 mm.) for 24 hr. The desired ketone, obtained as a viscous oil which did not crystallize upon standing, was employed directly below.

***p*-Anisyl Di(*p*-anisyl)methyl Ketoxime-C^{14} (IX).**—The oily ketone obtained from 21.1 g. of the above ketone anisolate was dissolved in a mixture of ethanol (65 ml.) and pyridine (14 ml.). The solution was treated with hydroxylamine hydrochloride (7.1 g.) and heated under reflux for 5 hr. then was chilled overnight, affording 18.7 g. of crude ketoxime. Four recrystallizations of this material from a 3:1 mixture of ethanol and acetone gave a constant melting sample of IX, m.p. 133–135°. Since Sumrell and Goheen[24] report the m.p. of this product as 159–161°, the product was analyzed. The melting point discrepancy which we find is presumably due either to polymorphism or to our obtaining a different stereomer of the ketoxime in question.

Anal. Calcd. for $C_{23}H_{23}O_4N$: C, 73.19; H, 6.14; N, 3.71. Found: C, 72.94; H, 6.18; N, 3.91. Radioactivity assay, 2.627 ± 0.004 mc./mole.

Alkaline Degradation of Phenyl Benzhydryl Ketone-C^{14}.—The procedure employed was essentially that of Blitz.[10,19,26] Sodium ethylate, prepared by dissolving sodium (5.0 g.) in absolute ethanol (50 ml.), was added to phenyl benzhydryl ketone-C^{14} (1.00 g., specific radioactivity 1.801 mc./mole) and the solution was heated under reflux for 5 hr. Water (40 ml.) was added and the ethanol was removed by distillation. The aqueous residue was extracted with ether and the extract was washed with water and dried over magnesium sulfate. Solvent removal left 0.625 g. (101%) of crude diphenylmethane. The above methanol distillate was added to four times its volume of water, and the mixture was extracted with ether, affording an additional 0.061 g. of diphenylmethane. The combined products were chromatographed (benzene) on 35 g. of neutral alumina (Activity II), yielding 0.539 g. (87%) of diphenylmethane whose infrared spectrum was identical with that of an authentic sample. The product was converted to its crystalline tetranitro derivative by the method of Matsamura,[27] nitrating with potassium nitrate (0.54 g.) in sulfuric acid (7.5 g.). The crude product, purified by leaching with boiling ethanol (4 ml.) and recrystallizing from acetic acid (8 ml.), gave pure di(2,4-dinitrophenyl)methane (63%), m.p. 172.5–174°, in agreement with the literature value,[27] m.p. 173°. Radioactivity assay, 0.0013 mc./mole.

The above alkaline residue was acidified with hydrochloric acid and extracted with ether. The extract was dried over magnesium sulfate, filtered and stripped of solvent to yield 0.425 g. (95%) of crude benzoic acid, which was recrystallized twice from water and sublimed to give pure benzoic acid, m.p. 121.5–122.5°, radioactivity assay 1.802 mc./mole. The above experiment indicates that phenyl benzhydryl ketone-C^{14} can be quantitatively degraded with sodium ethylate without rearrangement, providing an alternative method to that previously employed[2] for the degradation of this ketone.

Alkaline Degradation of *p*-Anisyl Di(*p*-anisyl)methyl Ketone-C^{14} (VIII).—VIII (1.00 g.) was dissolved in absolute ethanol (2 ml.) and treated with a solution of sodium (5 g.) in absolute ethanol (50 ml.) as above. The mixture was heated under reflux for 24 hr., treated with water (40 ml.), and processed as above. The neutral extract afforded 0.74 g. of an oil which solidified upon standing. This was chromatographed as before, yielding 0.57 g. (90%) of di(*p*-anisyl)-methane which was recrystallized from *n*-hexane, m.p. 51–52.5° in agreement with the reported value.[28] Acidification of the basic solution as before yielded 0.264 g. (63%) of crude *p*-anisic acid. Recrystallization and sublimation afforded a purified sample having m.p. 180–182° in agreement with the recorded value[29] of 184°.

As a further test of the efficacy of this degradation a mixture of *p*-anisic acid (0.40 g.) and di(*p*-anisyl)methane (0.54 g.) was dissolved in absolute ethanol (50 ml.) containing sodium (5 g.). The mixture was heated under reflux for 24 hr. and processed as above, yielding samples of *p*-anisic acid (0.39 g., 98%) and di(*p*-anisyl)methane (0.51 g., 93%) whose infrared spectra were identical with those of authentic samples.

Similar results were obtained when this degradation was applied to the above *p*-anisyl di(*p*-anisyl)methyl ketone-C^{14} (VIII). The di(*p*-anisyl)methane from this degradation proved to be nonradioactive, establishing the radiochemical structure of this ketone.

1,2,2-Tri(*p*-anisyl)ethylamine-1-C^{14} (VI).—A refluxing solution of *p*-anisyl di(*p*-anisyl)methyl ketoxime (5 g.) in absolute ethanol (100 ml.) was treated with finely cut sodium (10 g.) and additional ethanol (15 ml.) (near the end of the addition). When the sodium had dissolved water (500 ml.) was added and the ethanol was distilled *in vacuo*. The aqueous residue was extracted with ether and the extract was washed and dried over magnesium sulfate. Solvent removal left an oil which was treated with 6 *N* hydrochloric acid (25 ml.) and benzene (25 ml.). Agitation caused 4.7 g. (89%) of crude 1,2,2-tri(*p*-anisyl)ethylamine hydrochloride to crystallize. Recrystallization with decolorization from water (100 ml.) containing hydrochloric acid (15 ml.) afforded 3.8 g. of purified amine hydrochloride. This was dissolved in sufficient hot water to retain solution upon cooling, and the solution was extracted with ether, clarified with Norit, made alkaline with sodium hydroxide, and extracted with ether. The extract was washed, dried, and stripped of solvent to produce crude amine (87%) which crystallized on stirring with *n*-hexane. The product was recrystallized four times from ethanol, m.p. 95.5–96.5°.

Anal. Calcd. for $C_{23}H_{25}O_3N$: C, 76.00; H, 6.93; N, 3.85. Found: C, 75.90; H, 6.93; N, 3.90.

When this reduction was repeated with 10.0 g. of the above radioactive ketoxime (IX), a 7.7-g. (73%) yield of 1,2,2-tri-(*p*-anisyl)ethylamine-1-C^{14} hydrochloride resulted. A portion of this was converted to the free amine VI which, upon purification, had m.p. 95.0–95.5° and a radioactivity assay of 2.592 ± 0.004 mc./mole.

Deamination of 1,2,2-Tri(*p*-anisyl)ethylamine-1-C^{14} (VI).

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—The hydrochloride of VI (1.00 g.) was dissolved in boiling water (25 ml.), and the cooled mixture was extracted with ether (10 ml.). The aqueous solution was clarified with Norit, brought to a volume of 50 ml., treated with glacial acetic acid (1.0 ml.), cooled to 5°, and finally treated dropwise with stirring with a solution of 2.2 g. of sodium nitrite in 22 ml. of water. After the addition the mixture was allowed to warm to room temperature and to stand for 1 hr., then was made alkaline with potassium hydroxide and extracted with ether. The extract was washed, dried over magnesium sulfate, and stripped of solvent to yield 0.87 g. of oil which was chromatographed (benzene) on 50 g. of neutral alumina (Activity II), affording 0.147 g. of yellow oil which partially crystallized and whose infrared spectrum was similar to that of tri(*p*-anisyl)ethylene. Elution with benzene-ether (4:1) yielded 0.59 g. (65%) of 1,2,2-tri(*p*-anisyl)-ethanol. Final elution with methanol yielded 0.151 g. of solid which was not characterized. Recrystallization of the alcohol fraction from *n*-hexane–chloroform (2:1) yielded pure 1,2,2-tri(*p*-anisyl)ethanol, m.p. 107–109° in agreement with the reported value.[30]

A similar procedure was employed, using proportional quantities, in the deamination of 7.7 g. of the above 1,2,2-tri(*p*-anisyl)ethylamine-1-C^{14} hydrochloride, affording 2.67 g. (38%) of purified 1,2,2-tri(*p*-anisyl)ethanol-1,2-C^{14} (X), m.p. 108–110.5°, specific radioactivity 2.583 ± 0.002 mc./mole.

Degradation of 1,2,2-Tri(*p*-anisyl)ethanol-1,2-C^{14} (X).—The above X (2.55 g.) was oxidized to 2.53 g. (99%) of radioactive *p*-anisyl di(*p*-anisyl)methyl ketone by the method of Sarett and co-workers,[20] using chromic acid (2.30 g.) and pyridine (23 ml.). The crude ketone, whose infrared spectrum was identical with that of an authentic sample, was degraded with sodium ethylate as described above, yielding 0.66 g. (62%) of crude *p*-anisic acid and 1.45 g. (91%) of crude di(*p*-anisyl)methane. The purified *p*-anisic acid had m.p. 180–182° and a radioactivity assay of 2.083 ± 0.003 mc./mole. The recrystallized di(*p*-anisyl)methane had m.p. 50.5–52° and a radioactivity of 0.432 ± 0.0002 mc./mole.

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Partial Rate Factors for Nitration of Fluoranthene[1]

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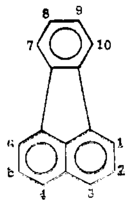
Nitration of fluoranthene gives the following partial rate factors relative to a 1-naphthalene position: in acetic anhydride at 0°: 1, 0.7; 3, 2.9; 7, 1.2; 8, 1.8; in acetic at 50°: 1, 0.3; 3, 8.1; 7, 0.6; 8, 2.7.

Dewar and co-workers[3] have determined the partial rate factors for nitration of a number of polycyclic aromatic hydrocarbons in acetic anhydride at 0°. These numbers have been useful for testing applications of molecular orbital theory to aromatic substitution[4]; however, the hydrocarbons studied were all of the alternant type for which all of the common molecular orbital reactivity indices are interrelated to a first approximation.[4] Such limitation does not extend to nonalternant hydrocarbons; hence, quantitative reactivity measurements for such compounds are particularly valuable for testing the various theories. We report the results of our study of the nitration of fluoranthene, I, a benzenoid but nonalternant aromatic hydrocarbon.



I

The nitration of fluoranthene has long been known to give predominantly 3-nitrofluoranthene, 3-II[5]; this isomer can be isolated readily in good yield.[6] von Braun and Manz[7] proved the presence of 8-nitrofluoranthene, 8-II, in the crude nitration product; however, only relatively recently has this isomer been isolated and characterized.[8] During the preliminary phases of our work, spectral comparisons of the product of nitration in acetic anhydride with 3- and 8-II indicated the presence of other isomers. Repeated chromatography of the nitration product on alumina eventually afforded two additional isomers in pure state, m.p. 144–144.5° and 150–151°.

Of the five possible mononitrofluoranthenes, four were known prior to our work. 1-Nitrofluoranthene 1-II, m.p. 151–153°, has been prepared by Campbell and Wilshire.[9] 2-Nitrofluoranthene, 2-II,

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[3] Summarized in M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

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[9] N. Campbell and J. F. K. Wilshire, *J. Chem. Soc.*, 867 (1954). Note that these authors use a different numbering system for fluoranthene and call this isomer the 2-nitro compound. This name was picked up by *Chemical Abstracts* where the compound is listed erroneously as "2-nitrofluoranthene" in both abstract and indices.