when admixed with an authentic specimen. The mixed melting point with triphenylmethoxysilane, m.p. 53–54°, was lowered to 38–45°.

Triphenylmethoxysilane.—To 0.1 g. (0.00435 g. atom) of sodium in 15 ml. of anhydrous methanol was added 1.28 g. (0.00435 mole) of triphenylchlorosilane. This mixture was refluxed for 10 minutes, during which time a white solid precipitated. The reaction mixture was then poured into 100 ml. of water and acidified with hydrochloric acid to pH 4. The oil which was present was thrice extracted with 10-ml. portions of chloroform which were dried over sodium sulfate. After removal of the chloroform the resulting oil was distilled and 0.88 g. (70%) collected which boiled over the range 166–168° at 1.3 mm. pressure. This oil solidified and melted at 51–53°. After recrystallization from petroleum ether (b.p. 60–70°) it melted at 53.5–54.5°.

Anal. Calcd. for $C_{19}H_{18}OSi$: Si, 9.68. Found: Si, 9.69.

Reduction of Methyl Triphenylsilanecarboxylate.—To 1.2 g. (0.0038 mole) of methyl triphenylsilanecarboxylate in 25 ml. of anhydrous ether was added 0.12 g. (0.0031 mole) of lithium aluminum hydride. After stirring for 3.5 hours, wet ether and then water were cautiously added, and the mixture was acidified with dilute hydrochloric acid. The ether layer was removed, dried with sodium sulfate, and evaporated to dryness under reduced pressure. The solid obtained was recrystallized from 15 ml. of petroleum ether (b.p. 60–70°) and the 0.75 g. (69%) of solid obtained melted at 109–111°. A mixed melting point with authentic triphenylhydroxymethylsilane, m.p. 109–111°, prepared by addition of triphenylsilylpotassium to formaldehyde,[9] was not depressed.

TORONTO, CANADA
AMES, IOWA

(9) H. Gilman and T. C. Wu, THIS JOURNAL, **76**, 2502 (1954).

A Carbon-14 Tracer Study of the Alkaline Rearrangement of Chlorophenanthraquinones[1,2]

BY DONALD G. OTT[3] AND GRANT GILL SMITH

The percentages of migration of the substituted rings in the alkaline rearrangements of 2-, 3- and 7-chlorophenanthraquinone-9-C^{14} were found to be 83.1, 66.8 and 79.8, respectively. A mechanism for the benzilic acid rearrangement is advanced based on the proposal that the migratory preferences are determined by the initial point of attack by hydroxide ion and not by the intrinsic migratory aptitudes of the aryl groups. Isotope effects of 1.09 and 1.12 were observed in the rearrangements of phenanthraquinones-9-C^{14} and of 2- and 7-chlorophenanthraquinone-9-C^{14}, respectively.

Although a number of substituted phenanthraquinones have been prepared and subjected to alkaline rearrangement since Baeyer[4] first reported the rearrangement of phenanthraquinone, no study of the migratory preferences in this rearrangement has been reported.

The migratory preferences of the chloro substituted rings with respect to the unsubstituted ring in the alkaline rearrangement of 2-, 3- and 7-chlorophenanthraquinone-9-C^{14} have been determined. These values are shown in Table I. The values 4.93 and 2.01 for the migratory preference ratios in 2- and 3-chlorophenanthraquinone-C^{14}, respectively, parallel the values obtained by Neville[5] for the analogous chlorobenzils: *m*-chlorobenzil, 4.10, and *p*-chlorobenzil, 2.05.[6] A study of the migratory preferences in the rearrangement of 1-chlorophenanthraquinone-9-C^{14} is reported elsewhere.[7]

The value of 1.09 ± 0.01 for migration of the identical unsubstituted rings in phenanthraquinone-9-C^{14} is a consequence of the isotope effect.

The migration ratios in the rearrangements of 2- and 7-chlorophenanthraquinone-9-C^{14} indicate an isotope effect of 1.12 ± 0.03.

TABLE I

MIGRATORY PREFERENCES IN THE ALKALINE REARRANGEMENT CHLOROPHENANTHRAQUINONES

| Compound	Counts/min., $BaCO_3$ plate[a]	Migration ratio subst./ unsubst.	Migration, % substd. ring
2-Chlorophenanthraquinone-9-C^{14}	2411 ± 11	4.93 ± 0.23	83.1
2-Chlorofluorenone-9-C^{14}	2158 ± 3	....	..
3-Chlorophenanthraquinone-C^{14}	756 ± 6	2.01 ± .03	66.8
3-Chlorofluorenone-9-C^{14}	543 ± 7	....	..
7-Chlorophenanthraquinone-9-C^{14}	1447 ± 11	3.95 ± .04	79.8
2-Chlorofluorenone-9-C^{14}[c]	315 ± 1	....	..
Phenanthraquinone-9-C^{14}	1112 ± 3	1.09 ± .01[d]	52.1[d]
Fluorenone-9-C^{14}	624 ± 3	....	..

[a] Plates of infinite thickness having an area of 2.4 cm.². [b] Ratio of the activity per labeled position of the fluorenone to the difference of the activities per labeled position of the phenanthraquinone and the fluorenone. Includes isotope effect. [c] Obtained from 7-chlorophenanthraquinone-9-C^{14}. [d] Isotope effect only.

The syntheses of the carbon-14 labeled chlorophenanthraquinones involved in this study were accomplished by methods such that the position of the chlorine substituents and the positions of the radioactive carbon atoms were unequivocably known.

(1) Presented in part before the Division of Organic Chemistry, 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15, 1953.

(2) Abstracted from a thesis presented to the Graduate Faculty of the State College of Washington by Donald G. Ott in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1953. Supported in part by a grant from the State College of Washington Isotopes Research Fund.

(3) Atomic Energy Commission Predoctoral Fellow, 1951–1953.

(4) A. Baeyer, *Ber.*, **10**, 123 (1877).

(5) M. T. Clark, E. C. Hendley and O. K. Neville, THIS JOURNAL, in press.

(6) The additional bond present in the phenanthraquinones appears to have little effect in determining the course of the rearrangement of these isomers.

(7) G. G. Smith and Donald G. Ott, THIS JOURNAL, **76**, 2342 (1954).

Conditions which are usually excellent for the rearrangement of benzils[8] are not applicable to the phenanthraquinone series since the alcohol used as solvent reduces the phenanthraquinones to phenanthrenequinhydrones. Therefore, the rearrangements were performed in aqueous 8.5% potassium hydroxide solution. 2-Chlorofluorenone and fluorenone were obtained from the corresponding phenanthraquinones in greater than 90% yields. In the case of the 3-chlorophenanthraquinone-9-C[14], however, the yield during the rearrangement was only 56%, and it was necessary to add dioxane in order to increase the speed of the reaction. Equations are shown below for the rearrangement of 2-chlorophenanthraquinone-9-C[14] (I) and subsequent oxidaation to the fluorenone (III).

The desired synthesis of 4-chlorophenanthraquinone was not accomplished thus making impossible a complete study of all the chemical isomers of chlorophenanthraquinone. 2-o-Chlorophenyl-α-toluic acid resisted the usual method of cyclization, even on prolonged reaction time. A higher boiling mixture of propionic acid and propionic anhydride with zinc chloride failed to cyclize the acid. Treatment with polyphosphoric acid[9] or with anhydrous hydrogen fluoride[10] also was unsuccessful. 4-Chlorophenanthraquinone has been prepared by another method,[11] but that synthesis involves procedures
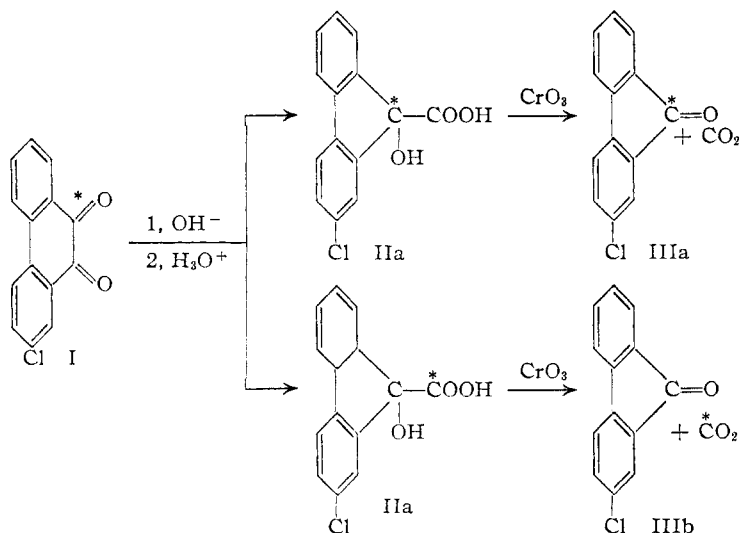

which do not permit specific orientation of the chlorine with respect to a radiocarbon atom in one of the carbonyl groups. Inspection of Fisher–Hirschfelder models indicates considerable steric hindrance of the chloro group in this series. Difficulties with this series might have been anticipated since some of the known 4-chlorophenanthrene derivatives exhibit anomalous solubilities and melting points in comparison with the other isomers.

Discussion of Results

The present investigation of the migratory pref-

(8) J. D. Roberts, D. R. Smith and C. C. Lee, This Journal, 73, 618 (1951).

(9) J. Koo, ibid., 75, 1891 (1953).

(10) W. S. Johnson, "Organic Reactions," Vol. II, ed. R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 157.

(11) A. I. Jakubowitsch and W. Worobjowa, J. prakt. Chem., 143, 281 (1935).

erence ratios involved in the alkaline rearrangement of chlorophenanthraquinones provides additional information regarding the benzilic acid rearrangement.[5,8,12-14] According to the Whitmore scheme, it would be interpreted that this reaction proceeds as
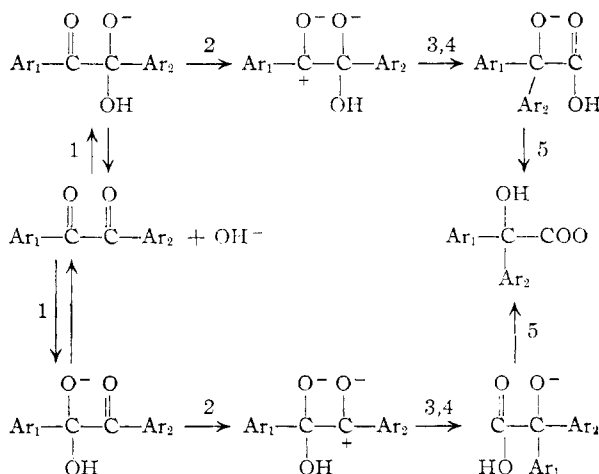
Westheimer[12] has demonstrated that the reaction is first order with respect to the concentration of benzil and also to that of hydroxide ion. Step 1 has been considered to be reversible by the oxygen-exchange experiments of Roberts and Urey.[13] Steps 2, 3 and 4 are the three steps of the Whitmore mechanism as outlined by Wheland.[14] The final step takes place as a result of the well-known difference in acidity between a carboxyl and a hydroxyl group. The migratory preferences in the benzil series are: p-anisyl, 0.46[5,8]; p-tolyl, 0.634[5]; p-chlorophenyl, 2.05[5] and m-chlorophenyl, 4.10.[5]

In the benzilic acid rearrangement, the group which migrates must necessarily be the group on the carbonyl-carbon atom attacked by the hydroxide ion. It is conceivable, however, if the slow step is the one in which the migration takes place,[13] that one of the two possible intermediates may be more apt to complete the rearrangement process than the other before reversal of hydroxyl ion attack takes place. If this were true, a group (e.g., p-anisyl) which has a high intrinsic migratory aptitude in a symmetrical pinacol rearrangement might be expected to increase the rate of rearrangement of a benzil. It has been demonstrated, however, that p-anisyl groups decrease the rate of a benzilic acid rearrangement; the bimolecular rate constants[15] for the alkaline rearrangement of benzil and of p-anisyl are 0.043 and 0.002, respectively. Further, the migratory preference (which is a ratio of the ratio of the rates of two competing reactions) of the

(12) F. H. Westheimer, This Journal, 58, 2209 (1936).

(13) I. Roberts and H. C. Urey, ibid., 60, 880 (1938).

(14) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 483.

(15) J. H. Blanksma and W. H. Zaaijer, Rec. trav. chim., 57, 883 (1938).

p-anisyl group in the benzilic acid rearrangement is less than that of the phenyl group.[8]

It appears, therefore, that the migratory preferences in the rearrangements of benzils are not determined during the migration step of the reaction, but rather by the relative electron densities on the two carbonyl-carbon atoms. The hydroxide ion would be expected to attack more readily that carbonyl group having the lower electron density. This argument is substantiated by the observation that the Hammett equation[16] applies to the migratory preferences in the rearrangement of the substituted benzils[5] and chlorophenanthraquinones. That the Hammett equation applies is not surprising if the migratory preference ratios are determined by hydroxide ion attack; it would be irrational, however, if migration depended only upon the intrinsic migratory aptitude of the migrating group.

It is proposed, therefore, that the following equations represent the reactions involved in the benzilic acid rearrangement
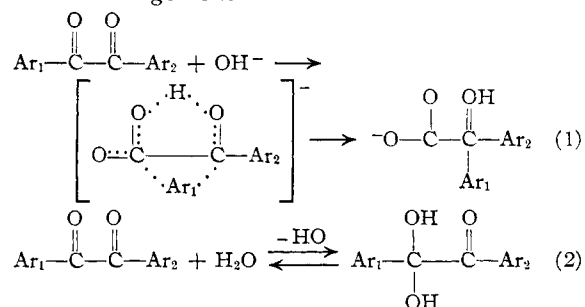
(An analogous series of reactions would take place if hydroxide ion attacked the other carbonyl-carbon atom.)

Reaction 1, which includes the three steps of the Whitmore mechanism, is a concerted, one-step process forming the rearranged product and is consistent with the observed second-order kinetics,[12] relative rates of benzil and *p*-anisil rearrangements,[15] Hammett equation correlations,[16] and migratory preferences of substituted benzils[5,8] and chlorophenanthraquinones.

Reaction 2 accounts for the observed oxygen exchange.[13] A similar reversible hydration reaction has been described by Bender[17] in a study of basic ester hydrolysis. The present investigation presents additional evidence of the well known isotope effect exhibited in carbon-14 containing compounds.[18] The magnitude of the isotope effect observed in the rearrangement of 2- and 7-chlorophenanthraquinone-9-C[14] (1.12 ± 0.03) and of phenanthraquinone-9-C[14] (1.09 ± 0.01) is similar to that noted by Stevens and Attree[19] in the rearrangement of carbonyl-labeled benzil (11.11 ± 0.01).

Experimental[20]

2-Chlorophenanthraquinone-9-C[14]. 2-Chloromethyl-4-

chlorobiphenyl.—2-Methyl - 4 - chlorobiphenyl (prepared from 2-methyl-4-chloroaniline in 18% yield, by the Gomberg–Bachmann coupling reaction[21]) (23.86 g., 0.118 mole) was dissolved in approximately 20 g. of carbon tetrachloride. This solution was treated with 15 g. (0.11 mole) of redistilled sulfuryl chloride and 0.1 g. of benzoyl peroxide.[22] The mixture was refluxed for five hours, then an additional 10 g. of sulfuryl chloride was added, and the mixture was maintained at approximately 50° overnight. The excess sulfuryl chloride and carbon tetrachloride were removed under diminished pressure; the residue was diluted with carbon tetrachloride, washed twice with water and dried over anhydrous magnesium sulfate. The starting material which was recovered on vacuum distillation was again subjected to chlorination. The total yield of product was 23.62 g. (85%), b.p. 117–118° (0.4 mm.),[23] m.p. 38–41°.

**2-Phenyl-5-chloro-α-toluic Acid-carboxyl-C[14].—The Grignard reagent was prepared in a nitrogen atmosphere from 10.0 g. (42.2 millimoles) of 2-chloromethyl-4-chlorobiphenyl, 2.0 g. (84 millimoles) of magnesium turnings and 80 ml. of anhydrous ether. Two of the three necks of the reaction flask were closed with standard-taper stoppers, a Tygon-covered magnetic stirring bar was introduced, and the flask was attached to a Grignard carbonation manifold similar to the type described by Calvin.[24] The reaction mixture was cooled to *ca.* −25° by means of a Dry Ice–Cellosolve-bath, and the system was evacuated through a water aspirator until the ether boiled vigorously. The system was closed, and the Grignard reagent was stirred magnetically while the carbonation was effected at a bath temperature of −20 to −25° with carbon dioxide generated within the apparatus; this was produced by the action of concentrated sulfuric acid on 10 g. (50 millimoles) of ordinary barium carbonate upon which had been placed a small porcelain boat containing 1 mg. of barium radiocarbonate.[25] The carbon dioxide generator was so arranged that the first drops of acid fell on the barium radiocarbonate; the radioactive carbon dioxide thus was swept into the Grignard reagent by the ordinary carbon dioxide which followed. The decomposition of the carbonate required about one hour; after this stirring was continued for an additional hour. Carbon dioxide was admitted to the system until atmospheric pressure was reached. The reaction flask was detached from the manifold, and a condenser was placed in the open neck of the flask. The reaction mixture was acidified with 3 *N* hydrochloric acid and, after reaction with the excess magnesium was complete, was extracted with three 20-ml. portions of ether. After the combined ether extracts had been washed with 25 ml. of water, the acid was extracted from the ether solution with three 10-ml. portions of 8.5% potassium hydroxide solution. The alkaline extract was washed with ether, acidified with 6 *N* hydrochloric acid and extracted with three 20-ml. portions of ether. The combined ether extracts were washed with water. After simultaneous treatment with charcoal and anhydrous magnesium sulfate, the solution was filtered through Celite filter aid, and the ether was evaporated under diminished pressure. The white powder which remained (7.80 g., 75%) was recrystallized from 60% benzene–ligroin (b.p. 50–60°); white needles, m.p. 113–114°.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: C, 68.20; H, 4.49. Found: C, 68.28; H, 4.23.

2-Chloro-9-phenanthryl Acetate-9-C[14].—To 3.0 g. (12.1 millimoles) of the above acid dissolved in 11 ml. of hot acetic anhydride was added a solution of 0.94 g. of freshly fused zinc chloride in 11 ml. of hot acetic acid.[26] The mix-

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 168.

(17) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

(18) G. A. Ropp, *Nucleonics*, **10**, No. 10, 22 (1952).

(19) W. H. Stevens and R. W. Attree, *J. Chem. Phys.*, **18**, 574 (1950).

(20) All melting points are corrected. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn. The yields given for the carbon-14 compounds are comparable to those obtained with non-labeled analogs.

(21) W. E. Bachmann and R. H. Hoffman, "Organic Reactions," Vol. II, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(22) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

(23) It was not found possible to distil this type of compound through either a glass helices packed column or an all-glass Dufton column without encountering flooding; consequently, none of the chloromethylbiphenyls were submitted for microanalysis.

(24) M. Calvin, *et al.*, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 179.

(25) The radioactive barium carbonate having a specific activity of 0.0315 mc. per mg. was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tenn., upon allocation of the Atomic Energy Commission.

(26) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **59**, 1028 (1937).

ture was refluxed for seven hours and a few milliliters of water was added cautiously through the reflux condenser to hydrolyze the excess acetic anhydride. The hot solution was poured into 75 ml. of water in a separatory funnel, and the white solid which precipitated was extracted with three 15-ml. portions of ether. The ether extracts were washed twice with water, twice with cold 8.5% potassium hydroxide solution and again with water. The ethereal solution was simultaneously treated with charcoal and anhydrous magnesium sulfate and filtered through Celite filter aid, and the ether was evaporated under diminished pressure. The light cream colored product was recrystallized from methanol to yield 2.75 g. (83%), m.p. 110–111.5°.

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: C, 70.98; H, 4.10. Found: C, 71.02; H, 4.16.

2-Chlorophenanthraquinone-9-C[14].—To 1.50 g. (5.5 millimoles) of the preceding ester dissolved in 6 ml. of acetic acid was added 1.75 g. of chromium trioxide in small portions over a period of one hour. The mixture was stirred, and a reaction temperature of *ca.* 85° was maintained during the addition. After standing overnight at 7°, the viscous green reaction mixture was filtered, and the solid was washed with acetic acid; yield was 1.08 g. (80%). A small sample was recrystallized twice from acetic acid; orange-red needles were obtained, m.p. 240–241°.[27]

Rearrangement of 2-Chlorophenanthraquinone-9-C[14].—The quinone (0.20 g., 0.8 millimole) was rearranged by stirring it in 20 ml. of 8.5% aqueous potassium hydroxide solution at *ca.* 85° for two hours. The solution was cooled, filtered into a separatory funnel through a sintered-glass funnel to remove a small amount of solid material and acidified with 6 N hydrochloric acid. The chlorobiphenyl-eneglycol acid was extracted with four 10-ml. portions of ether. The combined ether extracts were evaporated to dryness, and the residual semi-solid acid was oxidized by heating it on a steam-bath for one hour with 0.40 g. of chromium trioxide dissolved in 3 ml. of water and 6 ml. of acetic acid. The carbon dioxide released was swept with carbon dioxide-free air through a fritted-glass gas disperser into carbonate-free sodium hydroxide solution. The reaction mixture was diluted with 50 ml. of water, and the yellow precipitate was extracted three times with 20-ml. portions of ether. The ether extracts were washed twice with water, twice with 3 N sodium hydroxide solution and again with water. The solution, after simultaneous treatment with charcoal and anhydrous magnesium sulfate, was filtered through Celite filter aid into a tared flask. The 2-chlorofluorenone which remained (0.16 g., 93% yield) after evaporation of the ether was recrystallized twice from methanol to yield bright yellow needles, m.p. 124–124.5°.[28]

3-Chlorophenanthraquinone-9-C[14]. 2-Chloromethyl-5-chlorobiphenyl.—Chlorination of 2-methyl-5-chlorobiphenyl according to the procedure used for the 4-chloro isomer, produced this compound in a yield of 83%, b.p. 127–128° (0.8 mm.).

2-Phenyl-4-chloro-α-toluic Acid-carboxyl-C[14].—2-Chloromethyl-5-chlorobiphenyl (8.0 g., 34.7 millimoles) was converted to this acid, using the procedure given for the 5-chloro isomer, in a yield of 2.0 g. (32%).[29] Recrystallization from benzene gave white needles, m.p. 127–129°.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: C, 68.20; H, 4.49. Found: C, 67.77; H, 4.82.

3-Chloro-9-phenanthryl Acetate-9-C[14].—This compound was obtained from 1.15 g. of the corresponding α-toluic acid using the procedure given for the 2-chloro-isomer. The crude product was diluted with 0.78 g. of non-radioactive ester. Recrystallization of the mixture from methanol yielded 1.15 g. (46%) of white needles, m.p. 114–116°.

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: C, 70.98; H, 4.10. Found: C, 71.19; H, 4.22.

3-Chlorophenanthraquinone-9-C[14].—This quinone was prepared, using the procedure given for the 2-chloro-isomer, by chromic acid oxidation of 1.00 g. of 3-chloro-9-phenanthryl acetate. The quinone precipitated from the cold reaction

mixture to give 0.58 g. (65%) of orange powder, which produced, after recrystallization from glacial acetic acid, orange needles, m.p. 259–260°.[30]

Rearrangement of 3-Chlorophenanthraquinone-9-C[14].—3-Chlorophenanthraquinone-9-C[14] (0.18 g.) was heated on a steam-bath for nine hours with 15 ml. of 8.5% potassium hydroxide solution and 7 ml. of dioxane. 3-Chlorofluorenone, m.p. 157–158°[31] after recrystallization from methanol, was obtained in 56% yield (88 mg.).

7-Chlorophenanthraquinone-9-C[14]. 1-p-Chlorophenyl-2-methylcyclohexene.—The preparation of this compound was based on the procedure given by Orchin and Woolfolk[32] for the *o*-chloro-isomer.

In a 3-l. three-neck flask fitted with a Hershberg stirrer, reflux condenser, nitrogen inlet and dropping funnel, were placed 26.4 g. (1.1 moles) of magnesium turnings, a small iodine crystal, and 15 g. of *p*-bromochlorobenzene[33,34] dissolved in 50 ml. of anhydrous ether. After the reaction had started, *p*-bromochlorobenzene (a total of 206.7 g., 1.07 moles) in 600 ml. of anhydrous ether was added from the dropping funnel over a period of two hours. The mixture was refluxed an additional one-half hour. Thereafter, 104 g. (0.93 mole) of 2-methylcyclohexanone[35] was added over a period of two hours; slight cooling of the reaction flask was necessary. When approximately two-thirds of the ketone had been added, a thick, white precipitate separated which could be stirred only with a very efficient stirrer. Stirring was continued for three hours, and then the mixture was allowed to stand overnight. The complex was decomposed with 110 g. (2 moles) of ammonium chloride dissolved in 500 ml. of water. The ether layer was separated, and the water layer was extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, and the ether was distilled—the last under diminished pressure. To the crude, green 1-p-chlorophenyl-2-methylcyclohexanol was added 100 ml. of 85% formic acid. The mixture, after standing overnight, was heated and stirred on a steam-bath for three hours, and then it was transferred to a separatory funnel. Water was added, the lower layer of product was separated, and the aqueous layer was extracted with benzene. The benzene solution was washed with water, with 5% sodium bicarbonate solution and again with water; in turn it was dried over anhydrous magnesium sulfate. After filtration, the benzene was distilled, and the residue was fractionally distilled through a 15-cm. glass helices-packed column; this yielded 126.6 g. (66%) of 1-p-chlorophenyl-2-methylcyclohexene, b.p. 97–105° (0.44 mm.). A sample was redistilled for analysis[36]; b.p. 88° (0.28 mm.), n^{25}D 1.5616, d^{25} 1.136.

2-Methyl-4'-chlorobiphenyl.—To a mixture of 150 g. (0.61 mole) of chloranil[37] and 450 ml. of commercial xylene was added 60.0 g. (0.29 mole) of 1-p-chlorophenyl-2-methyl-cyclohexene. The mixture was refluxed for 12 hours and then cooled in ice. The solid chloranilhydroquinone was filtered and washed twice with xylene and twice with ligroin (b.p. 30–60°). (The yield of this reduction product was 102.5 g. (67%).) The xylene solution (the filtrate) was washed three times with water, three times with 150-ml. portions of 10% sodium hydroxide solution and again with water. After simultaneous treatment with charcoal and anhydrous magnesium sulfate, the solution was filtered through Celite filter aid, and the xylene was distilled. The residue was distilled and yielded 40 g. (68%) of crude product, which was dissolved in benzene, and the benzene solution was washed twice with cold concentrated sulfuric acid, three times with water, three times with 10% sodium

(27) J. Schmidt and E. Sauer, *Ber.*, **44**, 3241 (1911), reported m.p. 252°.

(28) I. M. Heilbron, D. H. Hey and R. Wilkinson, *J. Chem. Soc.*, 113 (1938), reported m.p. 123°.

(29) The low yield was attributed to the fact that the starting material had not been highly purified.

(30) H. Sandqvist and A. Hagelin, *Ber.*, **51**, 1523 (1918), reported m.p. 261°.

(31) I. M. Heilbron, D. H. Hey and R. Wilkinson, Ref. 28, reported m.p. 157°.

(32) M. Orchin and E. O. Woolfolk, THIS JOURNAL, **67**, 122 (1945).

(33) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 579.

(34) H. W. Schwechten, *Ber.*, **65**, 1605 (1932), reported 66–67°.

(35) G. G. Smith, Thesis, University of Minnesota, reported b.p. 64.5° (21.3 mm).

(36) Dr. H. W. Galbraith (private communication) reported: that he was unable to obtain consistent results in the elemental analysis of this compound.

(37) R. T. Arnold, C. Collins and W. Zenk, THIS JOURNAL, **62**, 983 (1940).

hydroxide solution and again with water. The solution was dried over anhydrous magnesium sulfate, filtered and subjected to vacuum distillation through a 15-cm. column of glass helices; yield 25.3 g. (43%) of 2-methyl-4'-chlorobiphenyl: b.p. 98–100° (0.45 mm.),[38] n^{20}D 1.5917, d^{25} 1.120.

Anal. Calcd. for $C_{13}H_{11}Cl$: C, 77.03; H, 5.47; Cl, 17.49. Found: C, 77.0; H, 5.61; Cl, 17.21.

2-Chloromethyl-4'-chlorobiphenyl.—Chlorination of 2-methyl-4'-chlorobiphenyl, according to the procedure used for the 4-chloro-isomer, yielded 84% of light-yellow product; b.p. 121–125° (0.45 mm.), m.p. 48–49°.

2-p-Chlorophenyl-α-toluic Acid-carboxyl-C¹⁴.—2-Chloromethyl-4'-chlorobiphenyl (10.0 g., 42.2 millimoles) was converted to this acid using the procedure given for 2-phenyl-5-chloro-α-toluic acid. Recrystallization of the crude product from benzene yielded 7.03 g. (68%) of white needles, m.p. 148.5–149°.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: C, 68.20; H, 4.49. Found: C, 68.43; H, 4.59.

7-Chloro-9-phenanthryl Acetate-9-C¹⁴.—From 3.50 g. (14.1 millimoles) of the acid, 1.16 g. (30% yield) of recrystallized product was obtained, m.p. 132–132.5°; the procedure used was that described for the 2-chloro-isomer. From the alkaline extract of the reaction mixture, 1.9 g. of starting material was recovered; this indicated a yield of 66% based on the acid which reacted.

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: C, 70.98; H, 4.10. Found: C, 70.85; H, 4.22.

7-Chlorophenanthraquinone-9-C¹⁴.—One gram (3.7 millimoles) of the preceding ester was oxidized in acetic acid with chromium trioxide by the same procedure as described for the preparation of 2-chlorophenanthraquinone-9-C¹⁴. A yield of 0.6 g. (67%) of quinone was isolated which produced bright orange-red needles, m.p. 240–241°,[27] on recrystallization from acetic acid.

Rearrangement of 7-Chlorophenanthraquinone-9-C¹⁴.—This quinone (0.30 g., 1.2 millimoles) was rearranged by stirring it in 30 ml. of 8.5% aqueous potassium hydroxide solution at *ca.* 85° for two hours. A yield of 0.25 g. (94%) of 2-chlorofluorenone-9-C¹⁴ was obtained from the reaction mixture in the same manner as was the 2-chloro-isomer. Two recrystallizations of the bright yellow compound from methanol gave yellow needles, m.p. 124–124.5°.[28]

Phenanthraquinone-9-C¹⁴.   1-(2-Tolyl)-1-cyclohexene.—This compound was prepared from *o*-bromotoluene[33] and cyclohexanone according to the procedure[32,39] given for 1-*p*-chlorophenyl-2-methylcyclohexene in 70% yield, b.p. 121–123° (16 mm.).[40]

2-Methylbiphenyl.—1-(2-Tolyl)-1-cyclohexene was dehydrogenated by the procedure given for 2-methyl-4'-chlorobiphenyl in 63% yield, b.p. 120–122° (11 mm.).[41]

2-Chloromethylbiphenyl.—Chlorination of 2-methylbiphenyl according to the procedure given for 2-methyl-4-chlorobiphenyl gave an 87% yield of product, b.p. 107–109° (0.55 mm.).[42]

o-Phenyl-α-toluic Acid-carboxyl-C¹⁴.—Using the procedure given for 2-*p*-chlorophenyl-α-toluic acid, 10.0 g. (49.2

millimoles) of 2-chloromethylbiphenyl was converted to *o*-phenyl-α-toluic acid-carboxyl-C¹⁴ in a yield of 7.21 g. (69%). Recrystallization from 70% benzene–ligroin (b.p. 30–60°) gave white needles, m.p. 114–115°.[43]

9-Phenanthryl Acetate-9-C¹⁴.—*o*-Phenyl-α-toluic acid was cyclized to this ester using the procedure given for the 2-chloro-isomer in a yield of 71%, m.p. 74–75°,[44] after recrystallization from methanol.

Phenanthraquinone-9-C¹⁴.—9-Phenanthryl acetate was oxidized to this compound according to the procedure given for 2-chlorophenanthraquinone in 50% yield, m.p. 202–204°,[45] after recrystallization from acetic acid.

Non-radioactive phenanthraquinone (0.58 g.) was added to an equal amount of the phenanthraquinone-9-C¹⁴, and the mixture was recrystallized for homogeneity; the product thus obtained was used in the rearrangement.

Rearrangement of Phenanthraquinone-9-C¹⁴.—Using the procedure given for the rearrangement of 2-chlorophenanthraquinone, fluorenone-9-C¹⁴ was obtained in 90% yield. Recrystallization from methanol yielded bright yellow needles, m.p. 83.5–84°.[46]

Attempted Synthetic Procedures Leading to 5-Chlorophenanthraquinone-9-C¹⁴.   2-o-Chlorophenyl-α-toluic Acid.—2-Chloromethyl-2'-chlorobiphenyl was prepared starting from *o*-bromochlorobenzene utilizing the procedure given for the preparation of 2-chloromethyl-4'-chlorobiphenyl. Carbonation of the Grignard reagent of this compound gave 2-*o*-chlorophenyl-α-toluic acid, m.p. 83–84°, in 58% yield after recrystallization from 30% benzene–ligroin (b.p. 40–60°). Recrystallization of a sample for analysis gave white needles, m.p. 84–84.5°.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: C, 68.20; H, 4.49. Found: C, 68.20; H, 4.62.

Attempted Cyclization of 2-o-Chlorophenyl-α-toluic Acid.—Several attempts were made to cyclize 2-*o*-chlorophenyl-α-toluic acid to the phenanthrene derivative from which 4-chlorophenanthraquinone might be prepared. Each attempt failed. They are as follows: treatment of the α-toluic acid with (a) zinc chloride, acetic anhydride and acetic acid under reflux for 19 hours, (b) zinc chloride, propionic anhydride and propionic acid under reflux, (c) polyphosphoric acid[9] for two hours at 100°, and again at 120° and (d) anhydrous hydrogen fluoride overnight.[10] In each case starting material was isolated.

Analytical Determinations.—Carbon-14 determinations were performed by wet combustion of the analytically pure organic compounds to carbon dioxide followed by conversion to barium carbonate plates of infinite thickness using standard procedures.[47,48] The amount of sample taken was calculated to yield the same weight of barium carbonate in each case. Counting of the plates was performed in a windowless flow counter operating in the Geiger region.[49]

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(49) We are indebted to Dr. G. A. Ropp, Chemical Division, Oak Ridge National Laboratory, for checking the radioactivities of some of the radioactive compounds.