Homolytic Aromatic Substitution. III.[1,2] Meerwein Arylation of Anthracene. A General Route to 9-Aryl- and 9,10-Diarylanthracenes[2,3]

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Meerwein arylation of anthracene has been found to afford a general homolytic route to 9-aryl- and 9,10-diaryl-anthracenes. Synthetic applications are illustrated by the preparation of previously unknown nitro derivatives of 9-phenyl- and 9,10-diphenylanthracene. Factors controlling yields and the functions of the copper salts are discussed.

A recent investigation of the mechanism of the classical type of Meerwein arylation reaction[4] disclosed that substitution of chlorobenzene or nitrobenzene for the usual substrate, a monomer, resulted in the formation of mixtures of isomeric biaryls having compositions characteristic of homolytic aromatic substitution.[5] These observations not only confirmed a radical mechanism for the Meerwein reaction but also established a new method of accomplishing homolytic aromatic substitution.[6] Selection of anthracene as the substrate for this investigation was prompted by the absence of a homolytic route to arylanthracenes and by the possibility of eventually obtaining reactivity data for this typical polycyclic aromatic hydrocarbon.[7,8]

Although the low solubility of anthracene in aqueous acetone precluded concentrations much above 0.02 M, normal Meerwein reaction conditions were employed: an aqueous solution of the diazonium chloride was added to an acetone solution of anthracene and cupric chloride. Initial experiments with four representative diazonium cations demonstrated conclusively that both 9-aryl- and 9,10-diarylanthracenes are major products of Meerwein arylations of anthracene (Table I). Synthesis of the previously unknown 9-p-nitrophenylanthracene suggested similar experiments with the isomeric diazonium salts and these reactions afforded the first samples of 9-o- and 9-m-nitrophenylanthracenes (Table II). Finally, a particular Meerwein arylation reaction, p-nitrophenylation, was investigated in some detail (Table III). The variation in yield of 9-p-nitrophenylanthracene and 9,10-di-p-nitrophenylanthracene with initial concentrations of diazonium salt indicates that the former compound is an intermediate in the formation of the latter. Confirmatory evidence for the occurrence of consecutive reactions are the Meerwein syntheses of 9,10-diphenylanthracene and of 9-phenyl-10-p-nitrophenylanthracene from 9-phenylanthracene and the corresponding diazonium chlorides. All com-

pounds prepared by the Meerwein reaction were identified by direct comparison with authentic samples or, for the nitro derivatives, by reduction and deamination to 9-phenyl- or 9,10-diphenylanthracene.

TABLE I

9-ARYL- AND 9,10-DIARYLANTHRACENES PREPARED FROM ANTHRACENE AND THE CORRESPONDING DIAZONIUM CHLORIDE BY MEERWEIN ARYLATION

Products (anthracenes)	Yield, %[a,b]
9-Phenyl-	(+)
9,10-Diphenyl-	(+)
9-p-Methoxyphenyl-	(+)
9,10-Di-p-methoxyphenyl-	18
9-p-Chlorophenyl-	(+)
9,10-Di-p-chlorophenyl-	37
9-p-Nitrophenyl-	11
9,10-Di-p-nitrophenyl-	62

[a] From 0.01 mole of anthracene and 0.10 mole of diazotized amine under standard reaction conditions; see Experimental section for details. [b] The (+) sign indicates that the specified compound was isolated.

TABLE II

9-NITROPHENYL- AND 9,10-DINITROPHENYLANTHRACENES PREPARED FROM ANTHRACENE AND THE CORRESPONDING DIAZONIUM CHLORIDE BY MEERWEIN ARYLATION

Products (anthracenes)	Yield, %[a,b]
9-p-Nitrophenyl-	21
9,10-Di-p-nitrophenyl	15
9-m-Nitrophenyl-	24
9,10-Di-m-nitrophenyl	11
9-o-Nitrophenyl-	(+)[b]
9,10-Di-o-nitrophenyl-	6

[a] From 0.01 mole of anthracene and 0.05 mole of diazotized amine under standard reaction conditions; see Experimental section for details. [b] Specified compound was isolated.

TABLE III

p-NITROPHENYLATION OF ANTHRACENE

Reactants, moles			Yield, %[a]	
Anthracene	p-Nitroaniline	CuCl₂	9-	9,10-
0.01	0.03	0.015	16	7
0.01	0.05	0.015	21	14
0.01	0.05	0.010	21	15
0.05	0.25	0.075	28	15
0.01	0.08	0.015		56,65
0.01	0.10	0.015	11	62,70

[a] Yields, based on anthracene, of 9-p-nitro- and 9,10-di-p-nitrophenylanthracenes.

Discussion

The mechanism suggested previously for the Meerwein arylation of monomers and simple arenes provides a basis for discussion of the present systems and an

(1) Paper II, S. C. Dickerman and G. B. Vermont, *J. Am. Chem. Soc.*, **84**, 4150 (1962).

(2) Paper I, a preliminary report of some of these results, S. C. Dickerman, L. B. Levy, and A. W. Schwartz, *Chem. Ind.* (London), 360 (1958).

(3) Financial support in the form of Frederick Gardner Cottrell Grants from the Research Corporation is gratefully acknowledged.

(4) The Meerwein arylation reaction has been reviewed recently: C. S. Rondestvedt, Jr., *Org. Reactions*, **11**, 189 (1960).
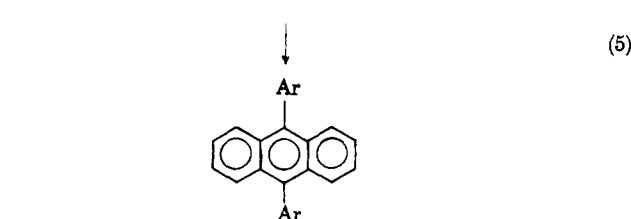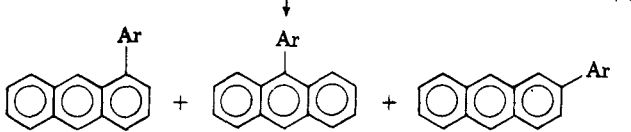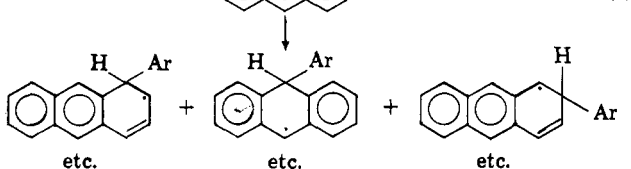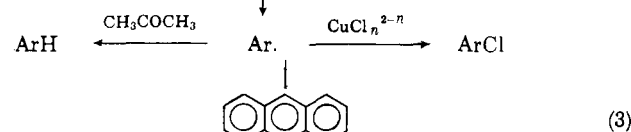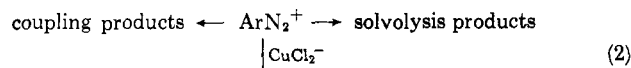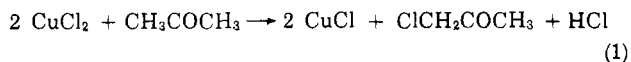
(5) S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1070 (1957).

(6) For a comprehensive review of this subject, see G. H. Williams, "Homolytic Aromatic Substitution." Pergamon Press, New York, N. Y., 1960.

(7) A prior study of the arylation of anthracene by what is now termed Meerwein arylation or reactions closely related to it had given only 9,10-diaryl derivatives: A. Etienne and C. Degent, *Compt. rend.*, **236**, 92 (1953); **238**, 2093 (1954).

(8) Peroxide phenylation of anthracene had been reported to afford only benzoyloxy derivatives: I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952)

appropriate modification of that mechanism is presented in the accompanying equations.[9] The reagent responsible for the homolytic decomposition of the diazonium salt is a complex ion of cuprous chloride, probably the dichlorocuprate I anion, which is generated *in situ* from acetone and cupric chloride (eq. 1).[9,10] Furthermore, it is now generally recognized that the Meerwein and Sandmeyer reactions possess a common initiation step, *i.e.*, the formation of aryl radicals by an oxidation–reduction reaction involving cuprous chloride and the diazonium ion.[9-12]

$$2\ CuCl_2 + CH_3COCH_3 \longrightarrow 2\ CuCl + ClCH_2COCH_3 + HCl \quad (1)$$

$$\text{coupling products} \longleftarrow ArN_2^+ \longrightarrow \text{solvolysis products} \quad (2)$$

(3)

(4)

(5)

Solvolysis and coupling reactions, *e.g.*, formazan formation, compete with the electron-transfer reaction and may consume a significant fraction of certain diazonium salts. Once formed, the aryl radicals become involved in competitive reactions, *i.e.*, ligand transfer, hydrogen abstraction, and addition to arene or monomer. Obviously the yield in any Meerwein reaction is a complex function of a number of variables including the reactivity of the substrate. However, the yields of 9,10-diarylanthracenes under identical reaction conditions (Table I) parallel the effects of substituents on the rate of the initial electron-transfer reaction, *i.e.*, p-NO$_2$ > p-Cl > p-OCH$_3$.[13,14] This correlation indicates that the effects of substituents in the diazonium ion on the yields in these and other Meerwein arylations of a specific substrate are largely

determined by the rate of formation of aryl radicals. If the electron-transfer reaction is rapid, *e.g.*, p-nitrobenzenediazonium ion, little diazonium salt is lost *via* coupling and solvolysis. Conversely, if aryl radical formation is inhibited by the substituent, *e.g.*, p-methoxy, diazonium salt will be consumed in side reactions.[15] The poor conversion of even the nitrobenzenediazonium salts to aryl- and diarylanthracenes is attributable to competing reactions involving the aryl radical and to the necessarily low concentration of anthracene in aqueous acetone.

Although 9-aryl- and 9,10-diarylanthracenes represent the major products of the reactions of aryl radicals with anthracene, the reactivity of this arene is not confined to the 9,10-positions. For example, the orientation pattern of anthracene in homolytic phenylation has been shown to comprise 84% 9, 14% 1, and 2% 2 isomer, respectively.[1] Furthermore, both *o*- and *p*-nitrophenylations of anthracene yield small amounts of the corresponding 1 and 2 isomers in addition to the 9-nitrophenylanthracene.[18] Thus, we infer that homolytic arylation of anthracene will in general afford isomeric arylanthracenes (eq. 3).

Participation by cupric copper in the reaction sequence leading to arylanthracene (eq. 4) is evidenced by the absence of detectable amounts of dimers (bianthryls) in Meerwein arylations and by previous observations that dimers are major products of the reactions of anthracene with 2-cyano-2-propyl,[19] methyl,[20] benzyl,[20] phenyl,[21] and "isoctyl" radicals,[22] all in the absence of copper salts. Significantly, the reactions of anthracene with phenyl radicals, generated from stabilized benzenediazonium salts with zinc dust (Waters reaction) in acetone has been reported to yield about equal amounts of 9,10-diphenylanthracene and 9,9',10,10'-tetrahydro-10,10'-dipheny-9,9'-bianthryl; 9-phenylanthracene was not isolated although its presence during reaction was inferred from the formation of 9,10-diphenylanthracene.[21] The divergent results of Meerwein and Waters arylations of anthracene have been interpreted in terms of the nature of the metal salts present; *i.e.*, there is no evidence that zinc salts participate in either ligand or one electron-transfer reaction.[1] Therefore the concentration of intermediate and relatively stable radicals, *e.g.*, 9,10-dihydro-10-aryl-9-anthranyl, will build up to the point where dimerization and, possibly, disproportionation become important competing reactions. In the presence of cupric chloride these intermediate radicals become oxidized to the corresponding isomeric arylanthracene and thus to potential substrates for further arylation. Preferential formation of 9,10-diarylanthracenes by a repetition of the proposed sequence is

(9) S. C. Dickerman, K. Weiss, and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); *J. Am. Chem. Soc.*, **80**, 1904 (1958).

(10) J. K. Kochi, *ibid.*, **77**, 5094, 5274 (1958).

(11) D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc.* (London) **A 242**, 16 (1957).

(12) The mechanism of the Sandmeyer and Meerwein reactions has been reviewed by H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 162–168.

(13) W. A. Coudrey and D. C. Davies, *J. Chem. Soc.*, S 48 (1949).

(14) These 9,10-diarylanthracenes are virtually insoluble in the reaction medium.

(15) The effect of the p-methoxy group is interesting in that p-methoxybenzenediazonium ion undergoes electron-transfer,[13] solvolysis,[16] and coupling[17] reactions less readily than the unsubstituted diazonium cation. In Meerwein p-methoxyphenylations of anthracene the slow disappearance of the diazonium salt, about 48 hr., is accompanied by the formation of products that impart an intense red color to the solutions. Presumably, formazan and/or diazo resin are produced.

(16) M. L. Crossley, R. H. Kienle, and C. H. Benbrood. *J. Am. Chem. Soc.*, **62**, 1400 (1940).

(17) J. B. Conant and W. D. Peterson, *ibid.*, **52**, 1220 (1930).

(18) S. C. Dickerman and M. Klein, unpublished results.

(19) A. R. Bickel and E. C. Kooyman, *Rec. trav. chim.*, **71**, 1137 (1952).

(20) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956); 1001 (1957).

(21) R. O. C. Norman and W. A. Waters, *ibid.*, 167 (1958).

(22) A. L. J. Beckwith, *ibid.*, 2248 (1962).

a direct consequence of the initial orientation which strongly favors the 9'isomers.[23]

Although Meerwein arylation provides a general route to 9-aryl- and 9,10-diarylanthracenes, its synthetic utility is impaired by the concurrent formation of isomeric products. For this reason alone it does not present an attractive alternative for those compounds that have or may be prepared by classical methods, e.g., the addition of organometallics to 9-anthrone or 9,10-anthraquinone followed by aromatization. However, homolytic arylation is at present the only route to mono- and dinitrophenyl derivatives of anthracene and, therefore, to a variety of previously unknown compounds.[24]

Experimental[25]

Reagents.—Eastman Kodak anthracene (480), Aldrich 9-phenylanthracene, and Merck alumina were used.

General Procedure for Meerwein Arylation of Anthracene.—A solution of 1.78 g. (0.01 mole) of anthracene and 2.55 g. (0.015 mole) of cupric chloride dihydrate in a mixture of 400 ml. of acetone and 40 ml. of water was prepared in a three-necked flask fitted with a sealed stirrer, a condenser, and a pressure-equalizing addition funnel. The condenser was attached to a simple gas buret and the apparatus was flushed with nitrogen or carbon dioxide. A solution of the diazonium salt, prepared from 0.05 mole of amine, 0.05 mole of sodium nitrite in 15 ml. of water, and 25 ml. of 6 N hydrochloric acid and filtered when necessary, was added rapidly and with vigorous stirring to the contents of the flask. The evolution of nitrogen varied from rapid and virtually quantitative for the nitrobenzenediazonium chlorides to slow and incomplete for diazotized p-anisidine. In any event, the reaction mixture was maintained at about 35° until the evolution of nitrogen ceased. After refrigeration overnight, any precipitate of diarylanthracene was collected by filtration and the filtrate was steam distilled. Experiments that involved smaller or larger amounts of diazonium salts were modified so that the total volume of water was 100 ml. for the former and 100–120 ml. for the latter. Reactions with larger amounts of anthracene represent simple multiples of these "standard conditions."

Phenylation of Anthracene.—The addition of 0.01 mole of diazotized aniline failed to yield a precipitate and the residue from steam distillation was dissolved in benzene. This extract was washed with dilute sodium hydroxide and water, dried, and chromatographed on alumina. The first five fractions off the column were combined and fractionally recrystallized from 1:1 benzene–ethanol to yield 9,10-diphenylanthracene of m.p. 244–248° (lit.[26] 249–250°). Addition of authentic 9,10-diphenylanthracene did not depress the melting point and the infrared spectra of the two samples were essentially identical.

The various solids and mother liquors from the fractional crystallization were combined and the solvents were removed under reduced pressure. The residue was dissolved in hexane chromatographed on alumina using hexane as developer and eluent. Fraction 3 off the column was recrystallized from ethanol and the first crop of crystals, mostly anthracene, was discarded. The second crop of crystals was recrystallized three times from ethanol and afforded 9-phenylanthracene, m.p. 149.5–150.5° (lit.[27] 152–153°). Addition of authentic 9-phenylanthracene did not depress the melting point and the infrared spectra of the two samples were virtually identical.

p-**Methoxyphenylation of Anthracene.**—Decomposition of the diazonium salt from 0.10 mole of diazotized p-anisidine gave 0.72 g. (18%) of product. Several recrystallizations from benzene afforded a sample of 9,10-di-p-methoxyphenylanthracene, m.p. 282–284° (lit.[26] 282°). Addition of authentic 9,10-di-p-methoxyphenylanthracene (m.p. 285–286°), prepared by the procedure of Ingold and Marshall,[26] did not depress the melting point and the infrared spectra of the two samples were virtually identical.

The residue after steam distillation was chromatographed in benzene on alumina and the colorless solids off the column were rechromatographed using hexane and alumina. The middle fraction off the column afforded a solid which was recrystallized several times from ethanol to give 9-p-methoxyphenylanthracene, m.p. 168–169° (lit.[28] 168.0–168.5°). Addition of authentic 9-p-methoxyphenylanthracene, prepared from 9-anthrone and p-methoxyphenyl lithium, did not depress the melting point and the infrared spectra of the two samples were identical.

p-**Chlorophenylation of Anthracene.**—Decomposition of the diazonium chloride from 0.01 mole of p-chloroaniline gave 1.46 g. (37%) of pale yellow needles, m.p. 288–305°. Several recrystallization from benzene–ethanol raised the melting point to 313–314° (lit.[26] 311°). Addition of an authentic sample of 9,10-di-p-chlorophenylanthracene[26] did not depress the melting point and the infrared spectra of the two samples were virtually identical.

Chromatography of the tarry residue from the steam distillation in hexane on alumina gave anthracene followed by colorless crystals, m.p. 168–174°. Recrystallization from a 4:1 mixture of acetone and water afforded 9-p-chlorophenylanthracene, m.p. 176.5–178.5° (lit.[29] 179–180°). Addition of authentic 9-p-chlorophenylanthracene, prepared from 9-anthrone and p-chlorophenylmagnesium bromide, did not depress the melting point and the infrared spectra of the two samples were essentially identical.

p-**Nitrophenylation of Anthracene.**—Addition and decomposition of a solution of p-nitrobenzenediazonium chloride from 0.10 mole of amine gave 2.17 g. (62%) of yellow solid. After recrystallization from pyridine, 9,10-di-p-nitrophenylanthracene was isolated as yellow needles, m.p. >400°, with decomposition (lit.[7] 457°).

Steam distillation of the reaction mixture followed by chromatography of the residue on alumina in a 1:1 mixture of hexane-benzene yielded 9-p-nitrophenylanthracene contaminated with p-chloronitrobenzene. Sublimation removed the latter compound leaving 0.320 g. (11%) of product. An analytical sample, bright yellow plates, m.p. 229–230°, was prepared by recrystallization from 1:1 benzene–ethanol.

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.29; H, 4.76; N, 4.57.

m-**Nitrophenylation of Anthracene.**—Decomposition of 0.05 mole of diazotized m-nitroaniline followed by concentration of the reaction mixture to three-quarters of the original volume gave 0.457 g. (11%) of pale yellow solid, m.p. 320–330°, with decomposition. Recrystallization from pyridine afforded 9,10-di-m-nitrophenylanthracene as off-white microcrystals, m.p. 344–345°.

Anal. Calcd. for $C_{26}H_{16}N_2O_4$: C, 74.28; H, 3.84; N, 6.66. Found: C, 74.05; H, 4.16; N, 6.91.

The remainder of the reaction mixture was processed in the usual manner and yielded 0.712 g. (24%) of 9-m-nitrophenylanthracene. Two recrystallizations from ethanol afforded an analytical sample of yellow plates or needles, m.p. 158–159°.

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.41; H, 4.43; N, 4.98.

o-**Nitrophenylation of Anthracene.**—Addition and decomposition of a solution of o-nitrobenzenediazonium chloride prepared from 0.05 mole of amine gave 0.257 g. (6%) of precipitate. After recrystallization from pyridine, 9,10-di-o-nitrophenylanthracene was isolated as yellow plates, m.p. 400°, with decomposition (lit.[7] 425°).[30]

Chromatography of the residue from steam distillation on alumina using 1:1 hexane–benzene gave a mixture of compounds

(23) Small amounts of what appear to be isomeric di-p-nitrophenyl-anthracenes and of a tri-p-nitrophenylanthracene have been isolated from Meerwein p-nitrophenylation of anthracene: S. C. Dickerman and A. A. Felix, unpublished results.

(24) For example, all structurally isomeric 9,10-dinitrophenylanthracenes and 9-methoxyphenyl-10-nitrophenylanthracenes have now been synthesized by Meerwein arylation: S. C. Dickerman, M. Klein, and G. B. Vermont, unpublished results.

(25) All melting points below 350° are corrected. The infrared spectra were determined with a Baird Model 4-55 spectrophotometer using potassium bromide wafers. The microanalyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(26) C. K. Ingold and P. G. Marshall, *J. Chem. Soc.*, 3080 (1926).

(27) P. L. Julian, W. Cole, G. Diemer, and J. G. Schafer, *J. Am. Chem. Soc.*, **71**, 2060 (1949).

(28) C. K. Bradsher and E. Faye Sinclair, *J. Org. Chem.*, **22**, 79 (1957).

(29) C. K. Bradsher and F. A. Vingiello, *J. Am. Chem. Soc.*, **71**, 1434 (1949).

(30) It is presumed that 9,10-di-o-nitrophenylanthracene can exhibit configurational isomerism due to restricted rotation. However, the configuration of the isolated compound has not been established.

from which 9-o-nitrophenylanthracene was isolated as yellow coralloid crystals or needles, m.p. 150–151°, by repeated recrystallizations from cyclohexane.

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68· Found: C, 80.45; H, 4.42; N, 4.79.

Reduction and Deamination of Nitrophenylanthracenes and Dinitrophenylanthracenes.—A solution or a suspension of 0.150 g. (0.005 mole) of the nitro or 0.210 g. (0.005 mole) of the dinitro compound in glacial acetic acid was treated with 0.791 g. or 1.582 g. of stannous chloride dihydrate and 0.5–1.0 ml. of concentrated hydrochloric acid. The mixture was heated on the steam bath with stirring until the characteristic yellow color of the nitro compound disappeared and then was concentrated under reduced pressure. The residue was digested with 5–10 ml. of concentrated hydrochloric acid and the solid was removed by filtration and diazotized in 5–10 ml. of 50% hypophosphorous acid.[31] After standing overnight, the reaction mixture was extracted with benzene and the extracts were concentrated and dried by distillation. Chromatography on alumina using hexane or a mixture of hexane and benzene gave the corresponding hydrocarbon. The yields of 9-phenylanthracene were 26% for the *ortho* isomer, 56% for the *meta*, and 15% for the *para* isomer while the yields of 9,10-diphenylanthracene amounted to 6%, 64% and 57% for the *ortho, meta*, and *para* isomers, respectively. After a single recrystallization, identity was established by mixture melting points and by comparison of the infrared spectra

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(31) N. Kornblum and D. C. Iffland, *J. Am. Chem. Soc.*, **71**, 2137 (1949).

of authentic 9-phenyl- and 9,10-diphenylanthracene with those of the experimental samples.

Phenylation of 9-Phenylanthracene.—Ten milliliters of an aqueous solution of benzenediazonium chloride prepared in the usual manner from aniline (0.700 g., 0.0075 mole) was added with stirring to a solution of 0.254 g. (0.001 mole) of 9-phenylanthracene and 0.170 g. (0.001 mole) of cupric chloride dihydrate in 40 ml. of acetone. Decomposition of the diazonium salt was accompanied by precipitation of a crystalline solid. After 2 hr. at 35°, the reaction mixture was cooled and 0.083 g. (25%) of 9,10-diphenylanthracene, m.p. 246–248° (lit.[26] 249–250°), was isolated by filtration. Identity was confirmed in the manner described previously.

p-Nitrophenylation of 9-Phenylanthracene.—An aqueous solution of *p*-nitrobenzenediazonium chloride, prepared in the usual manner from 4.14 g. (0.03 mole) of *p*-nitroaniline and diluted with water to a volume of 100 ml., was added with stirring to 2.54 g. (0.01 mole) of 9-phenylanthracene and 2.55 g. (0.015 mole) of cupric chloride dihydrate dissolved in 400 ml. of acetone. Decomposition of the diazonium salt afforded 2.04 g. (54%) of yellow solid, m.p. 282–290°. Recrystallization from benzene-ethanol gave yellow plates of 9-*p*-nitrophenyl-10-phenylanthracene, m.p. 296–297°.

Anal. Calcd. for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.57; N, 3.73. Found: C, 83.01; H, 4.67; N, 3.59.

Reduction, diazotization, and deamination of 0.300 g. (0.001 mole) of 9-*p*-nitrophenyl-10-phenylanthracene by the procedure described afforded 0.118 g. (58%) of 9,10-diphenylanthracene, m.p. 250–252° (lit.[26] 249–250°). Identity was confirmed by the usual methods.

Rearrangement of the 1,2,2-Triphenylethyl Radical

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2,3,3-Triphenylpropionaldehyde has been prepared by the lithium aluminum hydride reduction of *N*-(2,3,3-triphenylpropionyl)azridine. The *t*-butyl peroxide-catalyzed decarbonylation of this aldehyde in *o*-dichlorobenzene solvent at 155–185° yielded monomeric products (15%), consisting of 1,1,2-triphenylethane (95%) and triphenylethylene (5%), and a dimeric product (85%) whose infrared and n.m.r. spectra were in accord with those of 1,1,2,3,4,4-hexaphenylbutane. When the decarbonylation was conducted in the presence of thiophenol the yield of monomeric products increased to 37% and that of the dimeric product decreased to 22%. Uniquely labeled 2,3,3-triphenylpropionaldehyde-2-C^{14} was decarbonylated under similar conditions (thiophenol) and at several temperatures. Permanganate oxidation (not attended by subsequent phenyl migration) of the labeled 1,1,2-triphenylethane products afforded benzophenone samples whose radioactivity assays indicated that the intermediate 1,2,2-triphenylethyl radical had undergone 5% phenyl migration during decarbonylation at 155–165° and 14% at 176–184°. Subjection of 1,2,2-triphenylethane-1-C^{14} to the conditions of decarbonylation at 155–165° and 176–184° yielded samples of starting material, oxidative degradation of which indicated that 2.1% phenyl migration had occurred at the lower and 2.5% at the higher temperature. The oxidation of 1,2,2-triphenylethane-1-C^{14} to benzophenone using chromic oxide was attended by about 10% phenyl migration. Application of this degradation to the labeled 1,1,2-triphenylethane and 1,1,2,3,4,4-hexaphenylbutane products from the decarbonylation of 2,3,3-triphenylpropionaldehyde-2-C^{14} afforded benzophenone samples having identical radioactivity assays, suggesting that equivalent extents of phenyl migration had attended the oxidation of each hydrocarbon. The observed phenyl 1,2-rearrangement in the 1,2,2-triphenylethyl radical provides the second example of a radical 1,2-shift which is *not* accompanied by the formation of a more stable radical intermediate or by the relief of steric compression on the carbon atom adjacent to the radical site. The application of these techniques to the question of nonclassical, bridged radical intermediates is discussed.

Intramolecular rearrangements during free-radical reactions are neither so plentiful nor so extensively studied as those occurring during carbonium ion reactions. Several investigators have documented the tendency of 2-arylethyl radicals to undergo varying extents of aryl 1,2-migration, whether the radicals were produced by the action of cobaltous chloride and Grignard reagents on β-arylalkyl halides,[2-4] by the peroxide-

catalyzed decarbonylation of β-arylpropionaldehydes,[5-11] by the thermal decomposition of 2-arylethyl-azo derivatives,[12,13] during the addition of thiol com-

(2) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944).
(3) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).
(4) W. B. Smith and J. D. Anderson, *ibid.*, **82**, 656 (1960).
(5) S. Winstein and F. M. Seubold, Jr., *ibid.*, **69**, 2916 (1947).
(6) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).
(7) F. M. Seubold, Jr., *ibid.*, **75**, 2532 (1953).
(8) L. M. Slaugh, *ibid.*, **81**, 2262 (1959).
(9) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).
(10) J. W. Wilt and M. Philip, *ibid.*, **25**, 891 (1960).
(11) C. Rüchardt, *Ber.*, **94**, 2609 (1961).
(12) C. G. Overberger and H. Gainer, *J. Am. Chem. Soc.*, **80**, 4556, 4561 (1958).
(13) D. Y. Curtin and T. C. Miller, *J. Org. Chem.*, **25**, 885 (1960).