# The Reaction of Benzyl Radical Produced from Benzyl Chloride in the Presence of Iron and Water
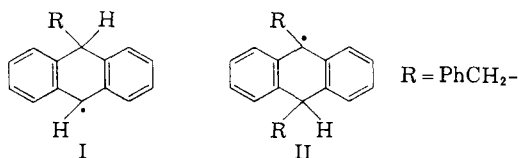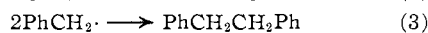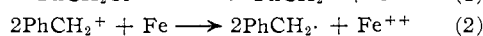
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Treatment of a mixture of benzyl chloride and anthracene with a suspension of iron powder in hot water gave 9,10-dibenzyl-9,10-dihydroanthracene and two isomers of 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl among other products. The reaction of tribenzyltin acetate with anthracene in boiling toluene afforded 9-benzylanthracene, 9,10-dibenzylanthracene and 9,9,10-tribenzyl-9,10-dihydroanthracene besides 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryls. These reactions are best interpreted by assuming the transient formation of benzyl radical as an intermediate.

Benzyl chloride and its derivatives are known to produce a bibenzyl compound under dehalogenation condensation upon treatment with a suspension of iron powder in hot water,[1] and this reaction has been utilized for preparing an artificial estrogen, hexestrol,[2] and its derivatives.[3]

Nothing, however, is known about the exact mechanism of this reaction. It appears plausible that the halide is transformed into a benzyl radical, presumably on the surface of iron, through reactions 1 and 2, which consist in the formation of benzyl cation, followed by the electron-exchange between the carbonium ion and the iron atom, the radical being then dimerized to form bibenzyl.

$$PhCH_2Cl \xrightarrow{Fe, H_2O} PhCH_2^+ + Cl^- \quad (1)$$

$$2PhCH_2^+ + Fe \longrightarrow 2PhCH_2\cdot + Fe^{++} \quad (2)$$

$$2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph \quad (3)$$



R = PhCH₂-

Another mechanism has been proposed in which the initial formation of organoiron compound and the subsequent condensation with the halide are postulated,[1b] but convincing evidence is lacking both for the transient formation of the organometallic compound and for the ionic character of the reaction. The present work has been carried out in order to prove or disprove the formation of the benzyl radical by attempting to trap this reactive intermediate with anthracene, which is known to act as an active radical-absorber. The *meso*-position of this hydrocarbon has been shown to be attacked by a number of radicals[4] including the benzyl radical itself.[5]

To a mixture of anthracene (about 10 mole % of the halide) and a large excess of reduced iron sus-

pended in water at 100° benzyl chloride was added dropwise and the reaction products were separated and purified by chromatography on activated alumina followed by recrystallizations. There were isolated toluene, benzyl alcohol, bibenzyl, anthraquinone, 9,10-bibenzyl-9,10-dihydroanthracene (III), and two isomers of 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl (IV), m.p. 227–228° and 238–240°, respectively.

The formation of these substituted anthracenes is best represented by the sequence of reactions postulated by Waters and his co-workers,[5] the benzyl radical as well as radicals I and II being active intermediates.

It has previously been discovered in this Laboratory that the reaction of benzyl chloride with tin powder suspended in hot water gives tribenzyltin chloride,[6] which can be converted into tribenzyltin acetate upon treatment with sodium acetate.[7] These organotin compounds have been found to be valuable stabilizing agents for poly-(vinyl chloride) plastics[8] and to form bibenzyl upon heating in the presence of silver acetate.[9] The thermal cleavage of tribenzyltin compounds appeared to be another source of the benzyl radical and the reaction with anthracene was investigated subsequently.

A mixture of tribenzyltin acetate, anthracene and silver acetate suspended in toluene was heated to reflux for three hours under stirring. The toluene-soluble products were separated and purified by chromatography over activated alumina. Thus were obtained bibenzyl, anthraquinone, 9-benzylanthracene (V), 9,9,10-tribenzyl-9,10-dihydroanthracene (VI) and 9,10-dibenzylanthracene (VII), besides IV and a tin-containing solid which did not melt below 285° and was not investigated further.

It is of interest to compare these results with those reported by Waters and his associates. The reaction of anthracene with benzyl radical produced from benzylmagnesium chloride under the catalytic action of cobaltous chloride in the presence of benzyl chloride[5a] has been described to give III, IV and a small amount of VII. On the other hand, the thermal decomposition of di-*t*-butyl peroxide in toluene[5b] has been reported to afford the benzyl radical which reacts with anthracene, giving VI and VII, besides III and IV.

(1) (a) Y. Ogata, T. Tsuruta and R. Oda, *Bull. Inst. Phys. Chem. Research (Tokyo, Japan)*, **21**, 616 (1942); *C. A.*, **43**, 2194 (1949); (b) Y. Ogata and H. Nakamura, *J. Org. Chem.*, **21**, 1170 (1956).

(2) (a) K. Sisido and H. Nozaki, THIS JOURNAL, **70**, 778 (1948); (b) K. Sisido, H. Nozaki and H. Kuyama, *J. Org. Chem.*, **14**, 1124 (1949); (c) Ng. Ph. Buu-Hoï and Ng. Hoán, *ibid.*, **14**, 1023 (1949).

(3) K. Sisido, H. Nozaki and Y. Udô, to be published.

(4) (a) I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952); (b) A. H. Turner and W. A. Waters, *ibid.*, 879 (1956); (c) A. L. J. Beckwith and W. A. Waters, *ibid.*, 1108 (1956); (d) R. O. C. Norman and W. A. Waters, *ibid.*, 167 (1958); (e) E. C. Kooyman, *Rec. trav. chim.*, **71**, 1137 (1952); **73**, 878 (1954); (f) L. F. Fieser and S. T. Putnam, THIS JOURNAL, **69**, 1038 (1947).

(5) (a) R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 950 (1957); (b) A. L. J. Beckwith and W. A. Waters, *ibid.*, 1001 (1957).

(6) K. Sisido and Z. Kinugawa, Japanese Patent Application, 0626, Dec. 23, 1953; *C. A.*, **49**, 4090c (1955).

(7) K. Sisido and Z. Kinugawa, Japanese Patent Application, 6428, Oct. 9, 1954; *C. A.*, **50**, 7856g (1956).

(8) K. Sisido and Z. Kinugawa, Japanese Patent Application 7889, Nov. 29, 1954; *C. A.*, **50**, 8250b (1956).

(9) K. Sisido and Y. Takeda, unpublished work.

The present observations on the reaction of benzyl radical produced in two different ways are parallel to these results. Thus, though VII could not be isolated in the reaction of benzyl chloride with iron powder suspended in water, the nature of the major products in this reaction is close to that of the "abnormal" Grignard reaction, *viz.*, the free radical I formed by the addition of the benzyl radical to anthracene is supposedly stabilized mainly through recombination with radicals. Another way of stabilization, *i.e.*, the abstraction of hydrogen atom from the initial free radical I and its analog II, appears to be common to both the thermal cleavage of tribenzyltin acetate and that of di-*t*-butyl peroxide in toluene, so that the observed formation of V, VI and VII is only conceivable by assuming this abstraction process being involved in the reaction sequence. It seems likely, in view of these results, that the potential hydrogen acceptors are not the benzyl radical itself but some other radicals of higher reactivity, for example, the tin-containing radical or *t*-butoxy one, etc.

Similar treatment of phenanthrene in place of anthracene with benzyl radical formed by the action of benzyl chloride on iron powder suspension as well as by the thermal cleavage of tribenzyltin acetate failed to give any condensation products containing the phenanthrene ring. The only identifiable product was bibenzyl in each case and most of the phenanthrene was recovered unchanged. Since the 9,10-positions of phenanthrene are known to be inactive to radical substitution but readily attacked by cationoid reagents, the observation also appears to favor the view that the above-mentioned reactions of anthracene are of radical nature. Thus, it can be safely concluded that the formation of bibenzyl upon treatment of benzyl halide with iron powder in hot water suspension occurs through benzyl radical as an intermediate.

## Experimental[10]

**Reaction of Anthracene with Benzyl Chloride in the Presence of Reduced Iron and Water.**—To a stirred suspension of 3.0 g. (0.017 mole) of anthracene[11] and 12 g. (0.214 g. atom) of reduced iron powder in 120 ml. of boiling water was added dropwise 25 g. (0.198 mole) of benzyl chloride in the course of 30 minutes under refluxing. After the addition was completed, stirring and refluxing were continued for an additional 5 hours. The reaction mixture was treated with 100 ml. of ether and filtered. The solids were dried and thoroughly extracted with hot benzene in a Soxhlet apparatus. Upon standing overnight at room temperature the ethereal solution deposited a crystalline product which was found to be the higher melting isomer of 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl. The details of identification are given below. The ethereal mother liquor was concentrated and the residue was fractionally distilled to give 0.1 g. of toluene which was identified as 2,4-dinitrotoluene, m.p. 70–71°. The higher boiling substances were combined with the evaporation residue of the benzene extract and the whole was subjected to fractional distillation under reduced pressure. There were isolated 9 g. of unchanged benzyl chloride, 3 g. of benzyl alcohol which was identified as *p*-nitrobenzoate, m.p. 85°, and 1.8 g. of bibenzyl, m.p. and mixed m.p. 52°. The distillation residue was treated with petroleum ether, whereupon 1.2 g. of unchanged anthracene was recovered as an insoluble solid.

The whole mother liquor was chromatographed on alumina and eluted with petroleum ether–benzene in successively increasing ratio of the latter and finally with ethanol. There were isolated the below-mentioned reaction products, besides an additional 1.2 g. of bibenzyl (from elution of petroleum ether) and 0.16 g. of anthraquinone (from final elution with ethanol), m.p. and mixed m.p. 275°.

**9,10-Dibenzyl-9,10-dihydroanthracene (III).**—Elution with 6:1 petroleum ether–benzene gave 0.6 g. (17% yield based on the consumed anthracene) of this hydrocarbon melting at 119° after recrystallizations from methanol, which afforded correct analyses of carbon and hydrogen and was dehydrogenated with sulfur to 9,10-dibenzylanthracene, m.p. 246–248° (lit.[5a] 248°).

**Isomeric 10,10'-Dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryls (IV).**—The hydrocarbon isolated prior to the chromatography was recrystallized from ethanol and then from benzene to give 0.2 g. (7% yield based on the anthracene consumed) of pure sample melting at 238–240°. Eluting the column with 2:1 petroleum ether–benzene gave 0.3 g. (11% yield based on the consumed anthracene) of a lower melting isomer, m.p. 227–228° after recrystallizations from a mixture of benzene and ethanol. Both of these compounds gave correct analyses of carbon and hydrogen and the same light absorptions (ethanol): $\lambda_{max}$ 243.2 ($\epsilon$ 1850), 248.7 (1990), 254.4 (2340), 260.6 (2090) m$\mu$.[12]

**Reaction of Anthracene with Tribenzyltin Acetate.**—A mixture of 2.0 g. (0.011 mole) of anthracene, 6.0 g. (0.013 mole) of tribenzyltin acetate, 2.0 g. (0.012 mole) of silver acetate and 50 ml. of toluene was heated under refluxing and stirring for 3 hours. After cooling, the mixture was filtered by suction and the residual solids extracted with benzene in a Soxhlet apparatus. The benzene solution was combined with the filtrate and concentrated. The crystalline solid which separated from the evaporation residue was recrystallized from ethanol and then from benzene to give 0.2 g. of 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl (m.p. 238–240°). The mother liquors were combined, evaporated and treated with petroleum ether. The insoluble solid was separated and treated with benzene to give 0.5 g. of unchanged anthracene. The petroleum ether solution was chromatographed on alumina in the same way as above. There were obtained 0.45 g. of bibenzyl (elution with petroleum ether), 0.4 g. (17% yield based on the consumed anthracene) of the lower melting isomer of 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl, m.p. 228–229°, an additional 0.15 g. (15% total yield based on the consumed anthracene) of its higher melting isomer, 0.1 g. of anthraquinone and 0.4 g. of tin-containing amorphous solid, m.p. above 285°, of unknown structure, in addition to the following hydrocarbons:

**9-Benzylanthracene (V).**—Elution with petroleum ether afforded 0.06 g. (3% yield based on the consumed anthracene) of this hydrocarbon, m.p. and mixed m.p. with authentic specimen 133°,[5b] after three recrystallizations from methanol and gave correct analyses for carbon and hydrogen.

**9,9,10-Tribenzyl-9,10-dihydroanthracene (VI).**—Elution with ethanol afforded 0.4 g. (11% yield based on the consumed anthracene) of VI melting at 175° (lit. 175°)[5b] after three recrystallizations of VI from the mixture of ethanol and a small amount of benzene. Analyses for carbon and hydrogen gave correct values; light absorptions (ethanol): $\lambda_{max}$ 265 ($\epsilon$ 1430) and 275.5 (861) m$\mu$.

**9,10-Dibenzylanthracene (VII).**—Elution with benzene afforded 0.2 g. (7% yield based on the anthracene) of VII in pale yellow needles, m.p. and mixed m.p. with authentic specimen[13] 248°, which gave correct analyses for carbon and hydrogen.

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(10) Analyses by Miss Kenko Ogawa. All temperatures are uncorrected.

(11) Anthracene was purified by three recrystallizations from benzene and one distillation with ethylene glycol and had m.p. 216°.

(12) While R. O. C. Norman and W. A. Waters (ref. 5a) recorded the isolation of three stereoisomers of IV melting at 238–240°, 227–229° and 182–183°, respectively, A. L. J. Beckwith and W. A. Waters described only two isomers melting at 252 and 178°, respectively, the lower melting isomer being found by the latter authors to be spontaneously converted into the higher melting one upon heating above its m.p. The present experiments coincide with the findings by Norman and Waters, though the lowest melting isomer has not been isolated.

(13) E. Lippmann and R. Fritsch, *Monatsh.*, **25**, 793 (1904).