Upon evaporation of the aqueous filtrate to dryness, 1.8 g. of a white substance was obtained. This substance, being insoluble in all common organic solvents and being soluble in hot water only, proved to be a hydrate of XXVII. Attempts to remove the hydrate water by heating the substance *in vacuo* resulted in partial decomposition of the material. Therefore for analysis the product was dried *in vacuo* for 1 hr. at 56°. It decomposed then in the melting point tube at 168–173°. The analysis of this sample indicated the presence of 2.5 moles of water.

Anal. Calcd. for $C_4H_5N_5O_2{\cdot}2.5H_2O$: C, 24.01; H, 5.04; N, 35.00. Found: C, 24.03; H, 5.51; N, 35.65.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1,4-Addition of Grignard Reagents to 9-Phenanthryl Ketones[1]

BY REYNOLD C. FUSON AND STANLEY J. STRYCKER

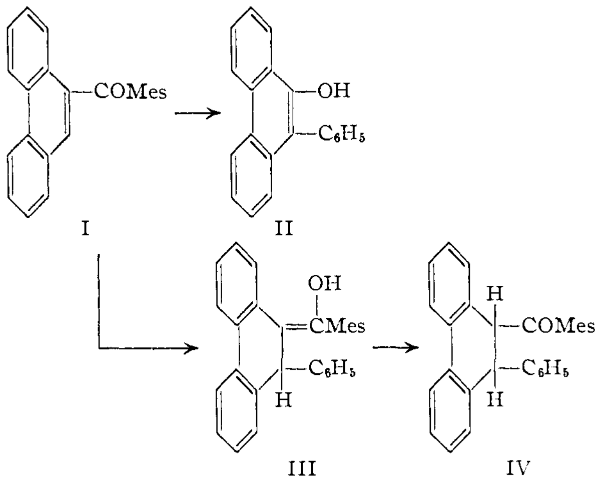
RECEIVED DECEMBER 20, 1956

It has been shown that 9-phenanthryl mesityl ketone reacts in the 1,4-manner with the methyl and phenyl Grignard reagents to give the corresponding 10-substituted 9,10-dihydrophenanthrenes. 9-Phenanthryl phenyl ketone and phenyl 9-phenanthrenecarboxylate react with phenylmagnesium bromide to yield phenyl 10-phenyl-9,10-dihydro-9-phenanthryl ketone.

The 1,4-addition of Grignard reagents to conjugated systems involving benzene rings, discovered 27 years ago by Gilman, Kirby and Kinney,[2] and almost at the same time by Kohler and Nygaard,[3] takes place more readily in the naphthalene series.[4] The difference, ascribed to the greater degree of double bond quality of the 1,2-bond in naphthalene, would be expected to be even more pronounced in suitably constituted phenanthrene derivatives; the 9,10-double bond of phenanthrene is known to have a higher order of reactivity than the bonds in naphthalene. To test this idea, we have prepared certain 9-phenanthryl ketones and subjected them to the action of Grignard reagents.

Our experiments have shown that mesityl 9-phenanthryl ketone (I) does react in the conjugate manner with the phenyl and methyl reagents. The first experiment with phenylmagnesium bromide gave an intractable oil. Chromatographic separation on an alumina-packed column yielded a small amount of the original ketone and a new compound which proved to be a phenol. It melted at 143–144° and formed an acetate (m.p. 153–155°) and benzoate (m.p. 179–180°). The melting points of the three compounds checked those given by Koelsch[5] for 9-phenyl-10-phenanthrol (II), its acetate and its benzoate. The formation of the phenanthrol is reminiscent of the production of 2-phenyl-1-naphthol in the naphthalene series[4] and similarly may be ascribed to the air oxidation of the enol III. In a subsequent experiment the expected dihydro ketones IV were isolated.

Methylmagnesium iodide behaved in a similar manner, the dihydro compound V likewise being obtained in two forms. Our belief that the methylated ketones are the expected diastereoisomers is strengthened by the observation that, when heated with a palladium-on-charcoal catalyst, the isomer having the lower melting point (109–110°) was changed to the higher-melting (154.5–155.5°) compound.



In search of a less highly hindered carbonyl compound we tried phenyl 9-phenanthroate (VI). With phenylmagnesium bromide it gave 9-benzoyl-10-phenyl-9,10-dihydrophenanthrene (VIII), presumably by way of 9-phenanthryl phenyl ketone (VII). This idea was supported by the results of experiments with the benzoyl compound VII. With the phenyl reagent it yielded the same dihydro ketone VIII obtained from the ester. We were satisfied with the structure VIII for this ketone, isolated in only one form, when we found that it could be dehydrogenated. The aromatized ketone, 9-benzoyl-10-phenylphenanthrene (IX), was obtained in small amount directly from the reaction mixture produced by the treatment of the phenyl ketone VII with phenylmagnesium bromide.

The aromatization could be effected in 76% yield by treatment of the dihydro ketone with bromine. This method was successful also in the aromatization of the methyl ketone V and the phenyl ketone IV. In the latter case, however, the dehydrogenation was accompanied by an unexpected cleavage. The cleavage product that was isolated proved to be 9-phenylphenanthrene. If mesitoic

---

[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U.S. Army (Contract No. DA-11-022-ORD-874).

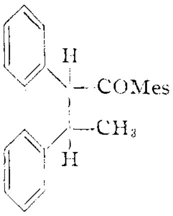
[2] H. Gilman, J. E. Kirby and C. R. Kinney, THIS JOURNAL, **51**, 2252 (1929).

[3] E. P. Kohler and E. M. Nygaard, *ibid.*, **52**, 4128 (1930).

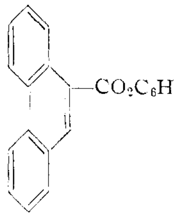
[4] R. C. Fuson, B. C. McKusick and F. W. Spangler, *ibid.*, **67**, 597 (1945).

[5] C. F. Koelsch, *ibid.*, **56**, 480 (1934).

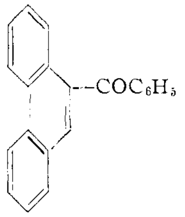
acid was formed also, as seems probable, it must have been retained by the alumina of the column employed in the chromatographic separation of the reaction mixture. This cleavage seems less strange in view of the discovery that certain cyclodehydration reactions, expected to yield 9-isopropylphenanthrene derivatives, were accompanied by loss of the isopropyl group.[6]



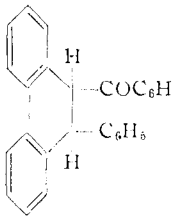
V



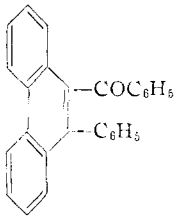
VI



VII

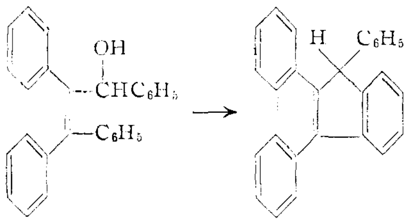


VIII



IX

Evidence for the structure of the benzoyl phenyl compound IX, and by analogy for the other products of 1,4-addition, was obtained by converting it to the known 9-phenyl-1,2,3,4-dibenzofluorene (XI). The ketone was reduced to the corresponding alcohol X which, as Koelsch[7] had shown earlier, was transformed to the fluorene by treatment with acetic acid containing a small amount of sulfuric acid.



X XI

9-Phenanthryl mesityl ketone was made by condensing 9-phenanthrylmagnesium bromide with mesitoyl chloride and also by the action of 9-phenanthroyl chloride on mesitylene in the presence of aluminum chloride. The preparation of 9-phenanthryl phenyl ketone from 9-cyanophenanthrene and the phenyl Grignard reagent was of especial interest since the nitrile itself might have reacted in the conjugate manner. However, chromatographic separation of the reaction mixture, after hydrolysis, gave no other phenanthrene derivative.

Experimental[8]

Phenyl 9-Phenanthroate (VI).—The procedure was similar to that employed earlier for the synthesis of phenyl 1-naphthoate.[9] A mixture of 12.9 g. of 9-phenanthroyl chloride and 5.1 g. of phenol was warmed to initiate the reaction. The evolution of hydrogen chloride continued for about 1 hr.; 60 ml. of methylcyclohexane was added and the mixture heated under reflux for 45 minutes. The hot mixture was filtered and the filtrate allowed to cool. The phenyl phenanthroate separated in the form of large clumps of colorless needles, m.p. 113.5–115.5°, yield 13.8 g. (85%). Recrystallization of the ester from ethanol raised the melting point to 115.5–116.5°.

Anal.[10] Calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.46; H, 5.01.

The infrared spectrum[11] contains absorption bands assignable to an ester function (1737 and 1200 cm.$^{-1}$) and a monosubstituted phenyl group (683 cm.$^{-1}$).

9-Benzoylphenanthrene (VII).—The procedure was patterned after that described for the preparation of 9-acetylphenanthrene.[12] A solution of 5.0 g. of 9-cyanophenanthrene in 50 ml. of dry benzene was added quickly to a Grignard reagent prepared from 19.3 g. of bromobenzene, 2.99 g. of magnesium and 200 ml. of ether. The dark, clear reaction mixture turned green and became opaque. During a 7-hr. period of reflux the color changed to a deep amber. The reaction mixture was cooled by means of an ice-bath, and an excess of dilute hydrochloric acid was added, with stirring. The initially formed yellow, fluffy precipitate changed suddenly to a milky white crystalline substance during the acidification. The precipitate was removed by filtration and warmed on a steam-bath for 4 hr. with distilled water. The crystalline material gradually changed to a clear oil, which settled to the bottom of the container. The oil, which was extracted with a mixture of ether and benzene, was subjected to chromatography. The 9-benzoylphenanthrene crystallized from high-boiling petroleum ether as colorless needles, m.p. 90–91°,[13] yield 5.3 g. (76%).

In the infrared spectrum a strongly conjugated carbonyl band appears at 1665 cm.$^{-1}$, a sharp peak at 701 cm.$^{-1}$ suggests the monosubstituted phenyl radical, and *o*-disubstitution of the phenanthrene nucleus is indicated by a sharp peak at 725 cm.$^{-1}$. A medium peak at 885 cm.$^{-1}$ may be assigned to the isolated hydrogen atom at the 10-position of phenanthrene.

9-Mesitoylphenanthrene (I). The Grignard Method.—The procedure described by Miller and Bachman[14] for 9-acetylphenanthrene was used as a pattern. The 9-phenanthrylmagnesium bromide, prepared from 71.0 g. of 9-bromophenanthrene, was added slowly to a solution of mesitoyl chloride in 250 ml. of anhydrous benzene. An immediate precipitate appeared and the mixture became warm. After completion of the addition, which required 30 minutes, the mixture was stirred at room temperature for an additional 3 hr. The 9-mesitoylphenanthrene, isolated by usual procedures, crystallized from benzene–ethanol, yield 71 g. (80%). It was purified by sublimation at 160° (1.5 mm.), m.p. 193.0–193.5°.

Anal. Calcd. for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.55; H, 6.18.

The infrared spectrum has bands attributable to a conjugated carbonyl group (1662 cm.$^{-1}$) and the mesityl radical (843 cm.$^{-1}$).

9-Mesitoylphenanthrene (I). The Friedel-Crafts Method.—The procedure was similar to that described for the preparation of 2-mesitoylnaphthalene.[4] One gram of anhydrous aluminum chloride was added to a mixture of 1.0 g. of 9-phenanthroyl chloride, 1.0 g. of mesitylene and 25 ml. of pure symmetrical tetrachloroethane, and the mixture was heated gently on a steam-bath for 2 hr. The dark solution was poured carefully into dilute hydrochloric acid, and

---

[6] C. K. Bradsher and D. J. Beavers, THIS JOURNAL, **78**, 3193 (1956).

[7] C. F. Koelsch, *ibid.*, **56**, 480 (1934).

[8] All melting points are corrected unless otherwise indicated.

[9] R. C. Fuson and F. W. Wassmundt, THIS JOURNAL, **78**, 5409 (1956).

[10] The microanalyses were performed by Mr. Joseph Nemeth, Mrs. R. Maria Benassi, Mrs. Lucy Chang, Mrs. Esther Fett, Mrs. Ruby Jo and Mr. Rollo Nesset.

[11] The infrared spectra were determined by Mr. James Brader, Mrs. Louise Griffing and Mrs. Beverly Thomas.

[12] J. E. Callen, C. A. Dornfeld and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 26.

[13] W. E. Bachmann, THIS JOURNAL, **56**, 1363 (1934).

[14] H. F. Miller and G. B. Bachman, *ibid.*, **57**, 766 (1935).

the solvent and unchanged mesitylene were removed by steam distillation. The crude product was boiled with methanol to which decolorizing carbon had been added and the mixture filtered. The ketone separated from the filtrate in beautiful, thin plates which had a yellow tinge, m.p. 187.5–189.5°, yield 0.96 g. (71%). It melted at 193.0–193.5° after sublimation. A mixture melting point with the product from the Grignard method showed no depression.

Condensation of Phenylmagnesium Bromide with Phenyl 9-Phenanthroate.—A solution of 5 g. of the ester in 75 ml. of dry benzene was added, over a period of 40 minutes, to a Grignard reagent made from 13.1 g. of bromobenzene, 2.02 g. of magnesium and 100 ml. of anhydrous ether. The reaction did not seem to be highly exothermic, and the solution slowly developed a green color. After being heated, under reflux and with stirring, for 17 hr., the mixture was treated with a saturated solution of ammonium chloride. The two-phase system, which had a marked odor of phenol, was stirred for 3 hr. The aqueous layer was extracted once with 150 ml. of ether and the ether solution added to the original organic layer.

Extraction of the organic layer with 10% sodium hydroxide removed phenol, which was isolated as 2,4,6-tribromophenol, m.p. 94–95°.[15] Steam distillation of the organic layer served to remove solvent and biphenyl. By recourse to chromatography 9-benzoyl-10-phenyl-9,10-dihydrophenanthrene was isolated which, after recrystallization from absolute ethanol, melted at 151.5–152.5°, yield 4.35 g. (72%).

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.78; H, 5.41.

The infrared spectrum contains significant bands at 2900, 1690, 747 and 695 cm.$^{-1}$ which are consistent with the structure assigned.

9-Benzoyl-10-phenylphenanthrene.—A solution of 0.45 g. of bromine in 50 ml. of carbon tetrachloride was added to a solution of 1.0 g. of the dihydro compound VIII in 50 ml. of carbon tetrachloride. The solution was maintained at reflux for 3 hr. at the end of which time the evolution of hydrogen bromide seemed to be complete. After being washed with a 10% solution of sodium bisulfite, the solution was freed of solvent by evaporation at reduced pressure. The clear colorless oil, left as a residue, was heated for 2 hr. with 150 ml. of dimethylaniline. The crude 9-benzoyl-10-phenylphenanthrene, isolated by pouring the previously cooled reaction mixture into dilute sulfuric acid, was recrystallized from 95% ethanol, m.p. 176–177°, yield 0.76 g. (76%).

Anal. Calcd. for $C_{27}H_{18}O$: C, 90.47; H, 5.06. Found: C, 90.38; H, 5.04.

The infrared spectrum contains bands attributable to a strongly conjugated carbonyl group (1670 cm.$^{-1}$), a monosubstituted phenyl radical (698 and 759 cm.$^{-1}$) and an *o*-disubstituted phenyl segment (724 cm.$^{-1}$). Moreover, aliphatic carbon–hydrogen bonds were indicated to be absent.

9-Phenyl-1,2,3,4-dibenzofluorene (XI).—A mixture of 0.19 g. of 9-benzoyl-10-phenylphenanthrene in 25 ml. of dry ether was warmed to effect solution, and to the solution was added slowly a slurry of 0.020 g. of lithium aluminum hydride in 10 ml. of ether. The mixture was heated on a steam-bath for 2 hr. and then treated successively with wet ether, aqueous ethanol and water. The gummy, viscous oil left by removal of solvent from the organic layer did not crystallize and was dissolved in 10 ml. of glacial acetic acid by warming. To the resulting solution were added 2 drops of concentrated sulfuric acid.[5] When the mixture was heated on the steam-bath, colorless crystals began to form immediately and the mixture soon appeared to be solid. The fluorene (0.14 g., 77% yield) crystallized from ethanol–toluene in the form of colorless, fluffy needles, m.p. 212–213°. The melting point given by Koelsch is 210–211°.

Anal. Calcd. for $C_{27}H_{18}$: C, 94.70; H, 5.30. Found: C, 94.48; H, 5.38.

The infrared spectrum has peaks suggesting the presence of an aliphatic hydrogen atom (2850 cm.$^{-1}$), monosubstituted benzene ring (698, 750 cm.$^{-1}$) and *o*-disubstitution (725 cm.$^{-1}$). The ultraviolet spectrum shows maxima at 247 mμ (log ε 4.92) and 322 mμ (log ε 4.48) with shoulders at 263 and 278 mμ.

Condensation of Phenylmagnesium Bromide with 9-Mesitoylphenanthrene.—Forcing conditions were employed and the entire experiment including the hydrolysis step was conducted in an atmosphere of nitrogen. A solution of 6.48 g. of the ketone in 75 ml. of dry benzene was added slowly to a Grignard reagent made from 6.28 g. of bromobenzene, 0.96 g. of magnesium and 50 ml. of anhydrous ether. The initial deep amber color changed to a deep green and, after the mixture had been heated for 6 hr. under reflux, was a milky yellow. At the end of a total reflux period of 8 hr., 80 ml. of 3 *N* hydrochloric acid was added and the two-phase system stirred overnight at reflux to effect ketonization. The organic layer, after being washed successively with water, 10% sodium bicarbonate solution and water, was dried over sodium sulfate. Removal of the solvent at reduced pressure left a yellow, viscous oil which crystallized slowly while being allowed to cool. Methanol removed the color, leaving the 9-mesitoyl-10-phenyl-9,10-dihydrophenanthrene as colorless crystals, m.p. 196–199°, yield 4.5 g. The compound was purified by recrystallization from chloroform–methanol, m.p. 202–203°.

Anal. Calcd. for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.51; H, 6.69.

Infrared analysis of the compound indicates the presence of a ketone function (1703 cm.$^{-1}$), the mesityl nucleus (852 cm.$^{-1}$), a monosubstituted phenyl radical (702 cm.$^{-1}$) and an *o*-disubstituted benzene ring (739 cm.$^{-1}$).

Chromatographic separation of the residue permitted the isolation of a white crystalline substance, m.p. 140.5–141.5°, the analysis of which is also in accord with the structure, 9-mesitoyl-10-phenyl-9,10-dihydrophenanthrene.

Anal. Calcd. for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.84; H, 6.71.

Except for minor shifts of certain bands, the infrared spectrum is the same as that of the higher-melting isomer.

In one experiment, in which two instead of five moles of Grignard reagent were used for each mole of ketone, the reaction product underwent oxidative cleavage—presumably at the enol stage. By chromatographic separation on alumina it was possible to isolate a compound which proved to be 9-phenyl-10-phenanthrol, which crystallized from aqueous methanol as transparent plates, m.p. 143–144°. It formed an acetate, m.p. 153–155°, and a benzoate, m.p. 177–179°. These values check those given by Koelsch.[5]

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.67; H, 5.13.

The infrared spectrum indicates not only the presence of a tertiary hydroxyl group (3530 cm.$^{-1}$) and of a monosubstituted phenyl ring (700 cm.$^{-1}$) but also the absence of aliphatic hydrogen atoms, of a carbonyl group and of a mesityl nucleus.

Condensation of Methylmagnesium Iodide with 9-Mesitoylphenanthrene.—A solution of 3.0 g. of the ketone in 75 ml. of dry benzene was added to a Grignard reagent made from 4.10 g. of methyl iodide, 0.70 g. of magnesium and 75 ml. of anhydrous ether. The reaction mixture immediately became dark green, but the color was gradually discharged during the subsequent 6-hr. period of heating the mixture under reflux. The two-layer system, produced by the addition of 75 ml. of 2 *N* hydrochloric acid, was heated under reflux for 13 hr. to ensure ketonization. An atmosphere of nitrogen was maintained throughout the experiment.

The organic layer was washed with water, with 10% sodium bicarbonate solution and again with water. The clear solution, after being dried overnight with anhydrous sodium sulfate, had a magenta color. Removal of the solvent left a pale yellow, viscous material which solidified when allowed to stand, m.p. 105–135°. Trituration of this solid with ether yielded a yellow oil and 1.4 g. of a white powdery solid, m.p. 152–155°, which proved to be the high-melting form of 9-mesitoyl-10-methyl-9,10-dihydrophenanthrene (V). It was purified by recrystallization from aqueous methanol, m.p. 154.5–155.5°.

Anal. Calcd. for $C_{25}H_{24}O$: C, 88.19; H, 7.11. Found: C, 88.11; H, 7.23.

The infrared spectrum shows bands attributable to a ketone group (1701 cm.$^{-1}$), the mesityl nucleus (853 cm.$^{-1}$) and an *o*-disubstituted benzene ring (740 and 760 cm.$^{-1}$).

---

[15] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systemic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 264 and 326.

The low-melting form of 9-mesitoyl-10-methyl-9,10-dihydrophenanthrene was obtained by submitting the ether-soluble portion of the product to a chromatographic separation on alumina. The major part of the material was eluted with a 10:1 ratio of cyclohexane to ether. Large needles, m.p. 109–110°, separated from a cooled aqueous ethanolic solution in a yield of 1.1 g.

Anal. Calcd. for $C_{25}H_{24}O$: C, 88.19; H, 7.11. Found: C, 87.83; H, 7.39.

The infrared spectrum of this compound is nearly superimposable on that of the higher-melting isomer.

Aromatization of 9-Mesitoyl-10-methyl-9,10-dihydrophenanthrene.—A solution of 0.24 g. of bromine in 10 ml. of carbon tetrachloride was added to 0.50 g. of 9-mesitoyl-10-methyl-9,10-dihydrophenanthrene dissolved in 25 ml. of carbon tetrachloride. The evolution of hydrogen bromide continued over a period of 5 hr. The reaction mixture was washed with sodium bisulfite and with water, and the solvent was removed. Chromatography of the pale yellow oil yielded a substance, m.p. 111–112°, which crystallized from ethanol. The combustion analysis agrees with that calculated for 9-mesitoyl-10-methylphenanthrene.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.33; H, 6.64.

The infrared analysis of this compound is consistent with this structure. A conjugated carbonyl group (1658 cm.$^{-1}$), the mesityl nucleus (854 cm.$^{-1}$) and characteristic aromatic peaks (757, 726 cm.$^{-1}$) are found in the spectrum.

Aromatization of 9-Mesitoyl-10-phenyl-9,10-dihydrophenanthrene.—A solution of 3.0 g. of 9-mesitoyl-10-phenyl-9,10-dihydrophenanthrene in 60 ml. of carbon tetrachloride was treated with 1.19 g. of bromine. The solution was heated gently until the evolution of hydrogen bromide was complete. Removal of the solvent left a dark oil, which was triturated with ethanol. Crystals separated from the cooled solution in the form of hexagonal plates, m.p. 160–161°, yield 1.7 g. This compound proved to be 9-mesitoyl-10-phenylphenanthrene.

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.67; H, 6.13.

The infrared spectrum of this compound contains peaks characteristic of a conjugated carbonyl group (1660 cm.$^{-1}$), the mesitylene radical (850 cm.$^{-1}$), *o*-disubstituted (725 cm.$^{-1}$) and monosubstituted benzene (699, 761 cm.$^{-1}$).

The ethanol filtrate yielded an oil which was subjected to chromatography. A hydrocarbon was isolated from the cyclohexane eluent. An aqueous acetic acid solution of this substance deposited a white crystalline material in the form of rosettes, m.p. 104–105°, yield 0.5 g. Its picrate melts at 113–114°. Koelsch[5] reports a melting point of 105–106° for 9-phenylphenanthrene and a melting point of 115° for its picrate.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.51; H, 5.53.

The infrared spectrum is consistent with a hydrocarbon structure. The only significant peaks of absorption which occur indicate monosubstituted benzene (700 cm.$^{-1}$) and aromatic vibrations (745, 725 cm.$^{-1}$). The ultraviolet spectrum exhibits a maximum at 254 mμ (log ε 4.95) which is characteristic of the phenanthrene nucleus.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

Alkylation of Benzene with Polyhalides in the Presence of Saturated Hydrocarbons and Aluminum Chloride[1]

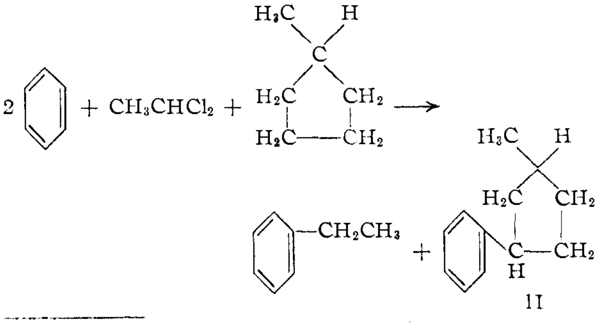
BY LOUIS SCHMERLING, ROBERT W. WELCH AND J. P. LUVISI

RECEIVED NOVEMBER 3, 1956

The aluminum chloride catalyzed condensation of a 1,1-dihaloalkane with benzene results in the formation of a primary alkylbenzene when the reaction is carried out in the presence of a hydrogen donor, namely a saturated hydrocarbon containing a tertiary carbon atom. Thus, for example, *n*-butylbenzene and (x-methylcyclohexyl)-benzene are produced in good yield by the reaction of benzene with 1,1-dichlorobutane in the presence of methylcyclohexane. Large amounts of hydrogen transfer products are also obtained with 2,3-dibromobutane and with 1,2-dichloro-2-methylpropane but not with 1,2-dichlorobutane. The mechanisms of these reactions and of the isomerization of tertiary alkylbenzenes is discussed.

In previous papers it was shown that excellent yields of primary monoalkylbenzenes (for example, isobutylbenzene[2] and 1-phenyl-3,3-dimethylbutane)[3] are obtained by the aluminum chloride catalyzed reaction of benzene with dichloroalkanes (1,2-dichloro-2-methylpropane and 1,1-dichloro-3,3-dimethylbutane, respectively) in the presence of a saturated hydrocarbon containing a tertiary carbon atom. The present paper describes the results of an investigation of the scope of this hydrogen transfer reaction, various polyhalides and saturated hydrocarbons being studied.

1,1-Dichloroethane.—The chief product obtained by the reaction of 1,1-dichloroethane with excess benzene in the presence of aluminum chloride at 3–4° was 1,1-diphenylethane (33% yield). Ethylbenzene was obtained in no more than 2% yield.[4] When the experiment was repeated, but with the addition of methylcyclopentane, practically no diphenylethane was produced. Instead, the chief reaction products were ethylbenzene and (methylcyclopentyl)-benzene isolated in approximately equal yields (42 and 38%, respectively) in accordance with the equation



II

---

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1956.

(2) L. Schmerling, R. W. Welch and J. P. West, THIS JOURNAL, 78, 5406 (1956).

(3) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, 77, 1774 (1955).

(4) Another product, 9,10-dimethyl-9,10-dihydroanthracene, isolated by previous workers was not obtained, presumably because of the large excess of benzene (6.2:1) over dichloroethane; *cf.* A. Angelbis and R. Anschütz, *Ber.*, 17, 165 (1884).