anhydride dissolved in 200 cc. of neutral alcohol and titrated with 0.1 N sodium hydroxide solution. To test the purity of the acid it was recovered and converted into phthalic anhydride. The quantitative isolation of the anhydride in this way was tested with a weighed sample which was converted into the salt, liberated and sublimed, and titrated. The recovery was 95.7%. In a second test a mixture of 1 g. each of the three phthalic acids gave a recovery of o-phthalic acid of 97%.

We were unable to find a quantitative method for the separation of isophthalic and terephthalic acids. As a consequence, the percentage of m-xylenes in the mixtures analyzed was considered to be the difference between the weights of the mixed xylenes and the sum of the ortho and para isomers. In several experiments the weight of m-xylene was calculated from the weights of the p-xylene and of the isophthalic and terephthalic acids obtained. The result checked within less than 1% the value obtained.

Summary

1. The effect of aluminum chloride on the three xylenes was studied under different conditions.

2. It was found that (1) change in temperature affects the relative proportions in which the isomers are formed; (2) rearrangement takes place much more rapidly than the decomposition of the hydrocarbons and yields a mixture approaching that present in commercial xylene; (3) decrease in the molecular ratio of aluminum chloride decreases the rate of rearrangement and the percentage decomposition; (4) the presence of ferric chloride had little or no effect and (5) hydrogen chloride did not affect rearrangement but appeared to increase decomposition.

Synthetic Experiments in the Chrysene Series

By Louis F. Fieser, Lloyd M. Joshel[1] and Arnold M. Seligman[2,3]

The goal of the present work was the development of a synthesis of 5-methylchrysene which would be capable of application as well to the synthesis of 4,5-dimethylchrysene, both hydrocarbons being desired as possible models of the carcinogenic 3,4-benzpyrene.[4] The scheme selected for investigation required 2-(α-naphthyl)-propionaldehyde (III) as an essential intermediate, and a method for the preparation of the aldehyde was found which is very satisfactory for the case at hand and which should be capable of other applications. The remainder of the plan could not be realized, for a rearrangement was encountered in the final stages of the synthesis.

In the most satisfactory procedure for preparing the intermediate aldehyde, α-naphthylmagnesium bromide was condensed with methoxyacetonitrile to give the keto ether I and this by interaction with methylmagnesium chloride was converted into the carbinol ether II in over-all yield of 80%. It is not practical to reverse the order of the two Grignard reactions, for when methylmagnesium chloride was added to methoxyacetonitrile ac-

cording to Gauthier[5] and the resulting methoxyacetone condensed with α-naphthyl Grignard reagent, the over-all yield of II was only 12%. Carbinol ethers analogous to II have been synthesized similarly by Bradsher and Schneider[6] from 2-iodobiphenyl and cyclized with acids to phenanthrene derivatives. Our methyl-methoxy-methyl-α-naphthylcarbinol (II) in the next step was distilled over potassium bisulfate, when methyl alcohol was liberated and the chief product was 2-(α-naphthyl)-propionaldehyde (III). This
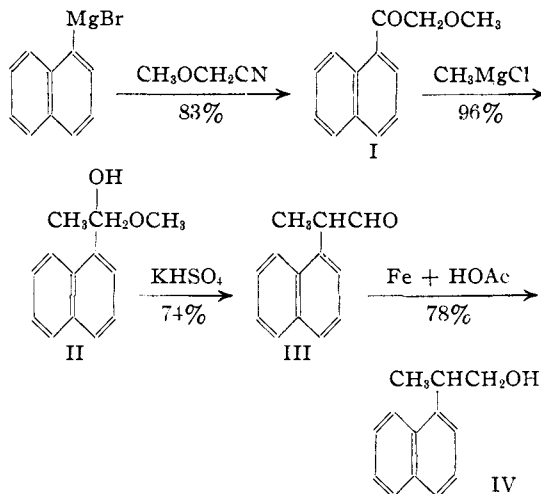
(1) Fellow of the Finney–Howell Research Foundation.

(2) George Cheyne Shattuck Memorial Fellow and Jeffries Wyman Scholar of the Harvard Medical School.

(3) The procedures for the synthesis of 2-(α-naphthyl)-propion-aldehyde and the corresponding alcohol were worked out originally by A. M. Seligman and the further experiments were all conducted by Dr. L. M. Joshel.

(4) Fieser and Seligman, This Journal, 60, 170 (1938).

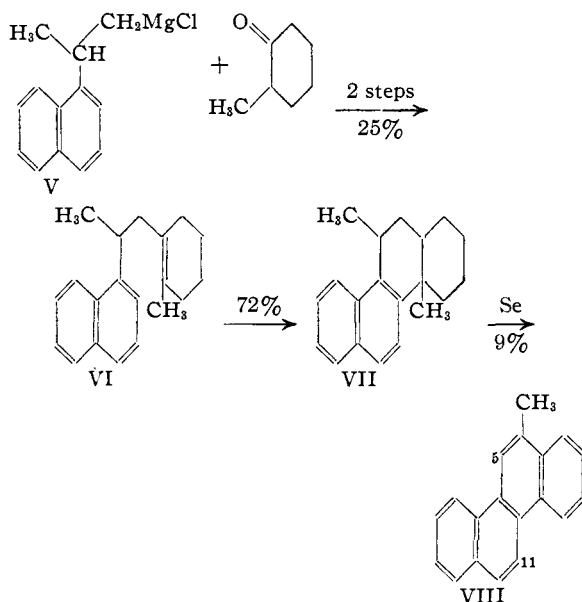(5) Gauthier, Ann. chim., [8] 16, 318 (1909).

(6) Bradsher and Schneider, This Journal, 60, 2960 (1938).

is probably formed by dehydration of II to the enol ether, $Ar(CH_3)C=CHOCH_3$, and acid hydrolysis to the enol form of the aldehyde. A small amount of the enol ether indeed escaped hydrolysis under the conditions used and was isolated as a by-product on purifying the aldehyde through the bisulfite compound. It is convertible into the aldehyde in good yield by hydrolysis with dilute hydrochloric acid.

2-(α-Naphthyl)-propionaldehyde, a liquid substance characterized as the crystalline semicarbazone, was reduced in good yield with iron powder and dilute acetic acid to the alcohol IV. Certain of the standard methods for conversion to the chloride or bromide gave mixtures of wide boiling range, but treatment of the alcohol with phosphorus pentachloride in benzene afforded a homogeneous chloride in fair yield. The chloride seems to have the expected normal structure, for carbonation of the magnesium derivative gave a substance corresponding in properties to the known β-(α'-naphthyl)-butyric acid.[7]

In one attempt to obtain 5-methylchrysene use was made of the Bogert–Cook synthesis and Cook's device of introducing a 2-methyl group in the alicyclic ring to suppress spiran formation, for this has been shown to give good results in the synthesis of chrysene itself.[8] The Grignard reagent (V) from 2-(α-naphthyl)-chloropropane was condensed with 2-methylcyclohexanone and the carbinol (oil) was dehydrated with potassium bi-

sulfate. This gave an unsaturated hydrocarbon of composition corresponding to VI, which was cyclized with aluminum chloride in carbon bisulfide solution at 0° to the dimethyloctahydrochrysene VII. Dehydrogenation with sulfur gave no pure product, but with either selenium or palladium charcoal there was obtained an oily product from which a homogeneous hydrocarbon was isolated in low yield through the trinitrobenzene derivative. The hydrocarbon, m. p. 159–159.8°, corr., has the expected composition but corresponds in properties to 6-methylchrysene (VIII), recently synthesized by Newman.[9] A direct comparison of the hydrocarbon, picrate (m. p. 170–170.6°, corr.), and trinitrobenzene derivative (m. p. 189.8–190.6°, corr.) with samples kindly made available by Dr. Newman established the identity of the substances, for the melting points are the same and there is no depression on mixing.

While it is not likely that Newman's synthesis could give anything but the expected 6-methylchrysene, there is analogy for the occurrence of a rearrangement in the dehydrogenation of a substance of the structural type involved in the present synthesis. Haworth[10] observed the para migration of a methyl group in the dehydrogenation of a 4-methyl-1,2,3,4-tetrahydrophenanthrene, but noted that rearrangement occurs only if the methylated ring is completely saturated. The nuclear methyl group of our hydrocarbon VII occupies a similar position in a saturated ring, and the case differs from that studied by Haworth only in that the para position is blocked. The most plausible interpretation of the present observation is that the methyl group migrates from C_5 to the ortho position 6. W. E. Jones and Ramage[11] recently investigated the dehydrogenation of certain decahydrochrysenes which normally should give 5-methylchrysene and 5,11-dimethylchrysene. They found the methyl groups to be largely eliminated from these positions with the formation of chrysene, but obtained from both starting materials small amounts of a methylchrysene, m. p. 151° (uncorr.?) which they tentatively regard as the 5-isomer. The apparently uncorrected melting points of their hydrocarbon, its picrate, and trinitrobenzene derivative are from 4 to 10° below the corrected melting points for corresponding compounds of the 6-methylchrysene series.

Before the above experiments were completed

(7) Radcliffe, Sherwood and Short, J. Chem. Soc., 2293 (1931).

(8) Cook, Haslewood and A. M. Robinson, ibid., 667 (1935).

(9) Newman, This Journal, 60, 2947 (1938).

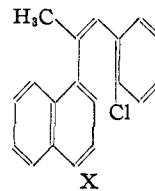(10) Haworth, Mavin and Sheldrick, J. Chem. Soc., 454 (1934).

(11) W. E. Jones and Ramage, ibid., 1853 (1938).

other possible synthetic routes were explored. 2-(α-Naphthyl)-propionaldehyde (III) was condensed with cyclohexylmagnesium chloride and the resulting carbinol IX (R = H) was submitted
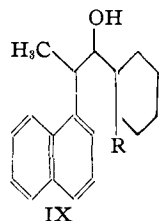
to cyclodehydration, both with phosphorus pentoxide and with potassium bisulfate, followed by aluminum chloride. In a closely analogous case, Perlman, Davidson and Bogert[12] obtained from benzylcyclohexylcarbinol a mixture of as-octahydrophenanthrene and the isomeric spiran. In our experiments the crude cyclization product on dehydrogenation with selenium afforded a hydrocarbon mixture from which there were separated as the trinitrobenzene derivatives small amounts of substances having the composition of a methylchrysene and of a spiran, respectively. Neither substance was obtained in large enough amounts for satisfactory purification and identification. Spiran formation was effectively suppressed by employing 2-methylcyclohexylmagnesium chloride in the synthesis, but the homologous carbinol (IX, R = CH₃) on cyclodehydration and selenium dehydrogenation gave a mixture containing chrysene and, in one experiment, a small amount of a substance which was not fully purified but which appeared from the analysis to be a methylchrysene. The partial loss of the methyl group corresponds to the experiences of W. E. Jones and Ramage,[11] and this synthesis clearly is not practical.

Another trial was inspired by Hewett's[13] successful utilization of a general synthetic method described in the patent literature.[14] 2-(α-Naphthyl)-propionaldehyde was condensed with the Grignard reagent from o-chlorobromobenzene and the crude carbinol was dehydrated by distillation over potassium bisulfate. The product was a liquid of the expected composition but boiled over a considerable range, and it presumably consisted of a mixture of the geometrical isomers of the structure X. Attempts to cyclize this sub-

(12) Perlman, Davidson and Bogert, J. Org. Chem., 1, 288 (1936).
(13) Hewett, J. Chem. Soc., 1286 (1938).
(14) British Patent 459,108; French Patent 807,704; American Patents 2,109,518, 2,109,833 [C. A., 31, 4136, 5814 (1937); 32, 3168, 3629 (1938)].

stance by fusion with potassium hydroxide alone[13] or in quinoline solution[14] gave only tars. The Grignard reagent from o-bromoiodobenzene was tried in the synthesis in the hope of obtaining a halide which would undergo cyclization more readily, but the carbinol was low in halogen content and no hydrocarbon was obtained on putting the crude material through the remaining steps of the above process.

Experimental Part[15]

Methoxymethyl α-Naphthyl Ketone (I).—The methoxyacetonitrile required was conveniently prepared by the action of cuprous cyanide on chloromethyl ether according to Gauthier.[16] Previous reports give the yield as 60–70%[16] and 74%[17]; by using a fused salt-bath to distil completely the product from the reaction mixture we obtained a yield of 81.6% of redistilled product, b. p. 120–120.6°.

A solution of 68 g. of methoxyacetonitrile in 300 cc. of benzene was dropped with stirring into a Grignard solution from 230 g. of α-naphthyl bromide and 27.5 g. of magnesium in 500 cc. of ether and 150 cc. of benzene. The mixture was refluxed for one-half hour and allowed to stand overnight. After decomposition with dilute hydrochloric acid the mixture was steam distilled for one hour and the residue taken up in ether, dried, and distilled. The ketone distilled as a viscous yellow oil, b. p. 144–146° (1 mm.) or 172° (4 mm.); yield 159.5 g. (83%).

Anal. Calcd. for C₁₃H₁₂O₂: C, 77.98; H, 6.04. Found: C, 77.77; H, 6.47.

The **semicarbazone**, prepared by refluxing a solution in alcohol with semicarbazide hydrochloride and sodium acetate, was crystallized from benzene and then from alcohol and formed colorless needles, m. p. 166.4–167.8°.

Anal. Calcd. for C₁₄H₁₅O₂N₃: N, 16.33. Found: N, 15.87, 15.94.

Methyl-methoxymethyl-α-naphthylcarbinol (II). (a) **From the Ketone I.**—A solution of 244 g. of the ketone in 500 cc. of ether was added during one hour to the Grignard reagent from 35 g. of magnesium and excess methyl chloride. The mixture was refluxed for one and one-half hours, allowed to stand overnight, and decomposed with acid. The ether layer was washed and dried and the product distilled, giving 254 g. (96.4%) of carbinol, b. p. 138–142° at 1.5 mm. The distillate partially crystallized in the receiver; a sample crystallized from petroleum ether in colorless prisms, m. p. 56.4–60.4°. The material analyzed was purified merely by distillation.

(15) All melting points are corrected. Microanalyses by Lyon Southworth, Herbert S. Wight†, and the Arlington Laboratories.*
(16) Gauthier, Compt. rend., 143, 831 (1906).
(17) Henze and Rigler, THIS JOURNAL, 56, 1350 (1934).

Anal.* Calcd. for C₁₄H₁₆O₂: C, 77.70; H, 7.46. Found: C, 77.69; H, 7.70.

(b) From Methoxyacetone.—In one trial the yield of methoxyacetone[5,17] from methoxyacetonitrile (67 g.) and methylmagnesium halide was 31% (b. p. 114°). Twenty-six grams of this reagent was added to a stirred Grignard solution from 70 g. of α-naphthylmagnesium bromide, and on proceeding as above there was obtained 26 g. (41%) of distilled carbinol.

2-(α-Naphthyl)-propionaldehyde (III).—A mixture of 160 g. of the carbinol II and 15 g. of fused potassium bisulfate was heated in a Claisen flask at 165–180° for one-half hour, allowing the volatile products to escape, and the residue was distilled at 2–4 mm. pressure. The clear distillate was stirred mechanically or shaken with 250 cc. of saturated sodium bisulfite solution, when a white precipitate of the addition product soon formed. After cooling, this was collected and washed with alcohol and ether. The aldehyde is conveniently stored in the form of this derivative; it is best liberated by shaking the bisulfite compound with aqueous sodium carbonate solution and extraction with ether. In the experiment cited there was obtained 83.5 g. (61%) of colorless aldehyde, b. p. 130–132° (2 mm.).

The **semicarbazone** formed colorless needles from alcohol, m. p. 203–204°.

Anal.* Calcd. for C₁₄H₁₅ON₃: C, 69.72; H, 6.27. Found: C, 69.95; H, 6.09.

On recovering the material in the alcohol–ether washings of the bisulfite compound there was obtained 23.4 g. (16%) of the **enol methyl ether** of the aldehyde as a pale yellow, unsaturated oil, b. p. 120–122° (1.5 mm.).

Anal. Calcd. for C₁₄H₁₄O: C, 84.81; H, 7.12. Found: C, 84.49; H, 7.19.

A 5.6-g. portion of this ether was refluxed with 50 cc. of 20% hydrochloric acid for three and one-half hours and the oil was extracted with benzene, washed, dried and distilled, giving 4.8 g. of crude aldehyde, b. p. 116–119° (1.5 mm.). On purification through the bisulfite compound and redistillation, 4.2 g. (81%) of pale yellow aldehyde, b. p. 117–119° (1.5 mm.), resulted. On this basis the total yield of pure aldehyde obtainable from the carbinol is 74%.

2-(α-Naphthyl)-propanol-1 (IV).—A mixture of 83.5 g. of the pure aldehyde III, 300 cc. of acetic acid, 300 cc. of water, and 200 g. of iron powder was heated with stirring on the steam-bath for seven hours. The solution was filtered hot and the filter cake was washed well with water and then with ether. The filtrate and washings were diluted with water and extracted with ether, and after evaporation of the solvent the remaining oil was refluxed for one-half hour with 15 g. of sodium hydroxide in 30 cc. of water and 50 cc. of alcohol to hydrolyze any acetate. The alcohol was then washed and dried in ether and distilled; it was obtained as a yellowish, viscous oil, b. p. 144–147° (3 mm.); yield 66.3 g. (78.5%).

The **3,5-dinitrobenzoate**, prepared by warming the alcohol with dinitrobenzoyl chloride, crystallized from alcohol in small, colorless needles, m. p. 125.5–126.5°.

Anal.* Calcd. for C₂₀H₁₆O₆N₂: C, 63.17; H, 4.24. Found: C, 63.16; H, 4.22.

Attempts to obtain a homogeneous halide from the alcohol II by the use of hydrobromic acid, phosphorus tribromide, thionyl chloride with pyridine or with dimethylaniline, or by the action of phosphorus pentachloride or tribromide on the acetate, all failed. Also unsuccessful were attempts to prepare the chloride by the condensation of naphthalene with allyl chloride[18] in the presence of sulfuric acid or anhydrous hydrogen fluoride; with the latter condensing agent (five hours at room temperature) there was obtained 13% of a halogen containing compound, but this had a wide boiling range (110–130° at 1 mm.). A satisfactory transformation of the alcohol was accomplished as follows.

2-(α-Naphthyl)-1-chloropropane.—A solution of 94 g. of the alcohol IV in 500 cc. of dry benzene was treated with 125 g. of phosphorus pentachloride, the vigorous reaction ensuing being controlled by external cooling. After refluxing for two hours the solution was cooled, water was added, and the benzene layer was washed, dried, concentrated, and treated with phosphorus pentoxide. Three distillations gave a mobile, yellowish liquid, b. p. 114–116° (1 mm.); yield 58 g. (56%). A sample shaken with 90% sulfuric acid and distilled was obtained in an almost colorless condition.

Anal. Calcd. for C₁₃H₁₃Cl: C, 76.28; H, 6.40. Found: C, 76.45; H, 6.41.

On preparing the Grignard reagent from 2.9 g. of the chloride and 0.4 g. of magnesium the reaction started promptly but about half of the metal remained unattacked after refluxing for several hours. On adding solid carbon dioxide and recovering the product in the usual way the acidic fraction afforded 1.1 g. (36%) of crude acid, m. p. 80–95°, on crystallization from benzene–ligroin. The recrystallized material formed colorless prisms, m. p. 108–108.6°, corresponding to the description of β-(α'-naphthyl)-butyric acid reported by Radcliffe, Sherwood and Short[7] (m. p. 108°).

2 - (α - Naphthyl) - 1 - (2' - methylcyclohexenyl) - propane (VI).—Difficulty was again experienced in effecting the conversion of 2-(α-naphthyl)-1-chloropropane (31.8 g.) into the Grignard reagent (with 4 g. of magnesium in ether-benzene), and titration showed only 40% active reagent. No better results were obtained on forming the reagent in the presence of 1 mole of ethyl bromide. The cooled solution was treated with 21 g. of 2-methylcyclohexanone, kept at room temperature for one hour, refluxed for three hours, stirred overnight, and then decomposed with ammonium chloride solution. The neutral portion was distilled, and after a large fore-run, 11.8 g. (27%) of a yellow, viscous oil was obtained at a bath temperature of about 250° (2 mm.). The carbinol could not be obtained crystalline.

For dehydration, 16.1 g. of the carbinol was heated with 25 g. of potassium bisulfate at 200° for one and one-quarter hours. After two distillations the hydrocarbon was obtained as a yellow, viscous oil boiling at about 200–225° (2 mm.); yield 14.2 g. (94%). The substance crystallized readily when triturated with methanol at −70° but melted below room temperature.

Anal. Calcd. for C₂₀H₂₄: C, 90.85; H, 9.15. Found: C, 90.59; H, 9.53.

(18) Truffault, *Compt. rend.*, **202**, 1286 (1936); **207**, 676 (1938).

5,10a-Dimethyl-*as*-octahydrochrysene (VII).—A solution of 13.5 g. of the olefin VI in 135 cc. of carbon bisulfide was treated at 0° with 15 g. of aluminum chloride in portions and stirred at 0° for twenty-one hours. The solution was decanted, washed with water, dried and evaporated, and the residue was distilled from a little sodium. Redistillation gave 9.7 g. (72%) of a viscous, almost colorless oil, b. p. about 220–240° (2 mm.). Tests with bromine and alkaline permanganate indicated that some unsaturated material was still present, but the tests were still positive after a further treatment with aluminum chloride as above at room temperature.

Anal.† Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.37; H, 8.94.

6-Methylchrysene (VIII).—The octahydride (2 g.) was heated with selenium (4.8 g.) at 320° for twenty-four hours and the product extracted with benzene, distilled, treated with norite in benzene, and distilled over sodium. The resulting oil yielded a crude but crystalline trinitrobenzene derivative from benzene, and after passing a benzene solution of this material through a tower of alumina the recovered hydrocarbon crystallized from benzene–alcohol as colorless plates, m. p. 141–148° (167 mg.). The combined product from two such runs was crystallized several times from ethyl acetate–alcohol and gave 165 mg. of colorless, fluorescent needles, m. p. 159–159.8°.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.19; H, 5.90.

The melting point of the hydrocarbon was not depressed by admixture with a sample of 6-methylchrysene synthesized by Newman.[9] This was true as well of the picrate, which crystallized from benzene–alcohol in orange needles, m. p. 169.8–170.2°, with previous softening, and of the trinitrobenzene derivative. The latter derivative, which has not been described before, was obtained from our hydrocarbon as yellow needles, m. p. 188.5–189.5°, from benzene–alcohol, and from Newman's sample of hydrocarbon as yellow needles, m. p. 189.8–190.6°.

Anal. Calcd. for $C_{25}H_{17}O_6N_3$: C, 65.93; H, 3.76. Found: C, 65.83; H, 4.02.

On heating 0.5 g. of the octahydride with 50 mg. of 30% palladium charcoal for sixteen hours at 310°, with the addition of 150 mg. more catalyst at intervals, the gas evolution was only 25% of the theoretical amount. The mixture was extracted with benzene and the hydrocarbon precipitated as the trinitrobenzene derivative. After recovery as before, one crystallization from benzene–ligroin gave 17 mg. of colorless needles, m. p. 145–150°; on recrystallization the substance melted at 154–158° and gave no depression when mixed with the above sample.

1-Cyclohexyl-2-(α-naphthyl)-propanol (IX, R = H).—A solution of 7.3 g. of freshly distilled 2-(α-naphthyl)-propionaldehyde in 40 cc. of ether was added to the ice-cold Grignard reagent from 5.8 g. of cyclohexyl chloride and 1.3 g. of magnesium. After one hour in the ice-bath, and one and one-half hours at room temperature, the mixture was refluxed for one hour and decomposed with ammonium chloride solution. The ether solution was washed and dried and the solvent displaced with petroleum ether, from which the carbinol crystallized in two crops as colorless needles, m. p. 55–58°; yield 6.5 g.

(61%). On recrystallization the substance melted constantly at 59–61°.

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.03; H, 9.00. Found: C, 84.64; H, 9.69.

Cyclodehydration of IX and Dehydrogenation.—For dehydration and ring closure the above carbinol (IX, R = H) was either heated with phosphorus pentoxide at 150° for thirty minutes or heated with potassium bisulfate at 160–180° for one hour, followed by treatment of the resulting oil with aluminum chloride in carbon bisulfide at 0° for twenty-four hours. In either case the oil was then heated with selenium at 320° for twenty-four hours and the product isolated as the trinitrobenzene derivative. The crude derivative from 2 g. of carbinol amounted to 363 mg. and melted at 90–100°. Fractional crystallization from alcohol gave 50 mg. of an orange substance, m. p. 232–235° with previous softening, having the composition of a methylchrysene-trinitrobenzene.

Anal.† Calcd. for $C_{25}H_{17}O_6N_3$: N, 9.23. Found: N, 9.27.

A yellow substance was also separated in small amounts from the mixture; this melted at 107–109° and the nitrogen content is that of a derivative of the **spiran** (or octahydride).

Anal.† Calcd. for $C_{25}H_{25}O_6N_3$: N, 9.07. Found: N, 9.09.

The preparation of **1-(2′-methylcyclohexyl)-2-(α-naphthyl)-propanol-1 (IX, R = CH₃)** from 2-methylcyclohexyl chloride[19] (6.6 g.) and the aldehyde III (7 g.) was conducted as before, the product remaining after evaporation of the washed and dried ether extract being a viscous yellow oil which failed to crystallize (stereoisomerism?); yield 8.3 g. (77%). In one trial 3 g. of the crude carbinol was dropped slowly with stirring and ice cooling into 6 cc. of 90% sulfuric acid and the dark, viscous mass was extracted with benzene. After washing with 85% sulfuric acid and water, and removing the solvent, a yellow, viscous oil (1.4 g.) distilled at a bath temperature of about 240° (2 mm.). This was heated with selenium as above and the purified product afforded 239 mg. of an orange mixture of trinitrobenzene derivatives, m. p. 155–162°, which could not be separated by crystallization. After decomposing the complex (alumina tower), crystallization from benzene–methanol afforded 42 mg. of **chrysene**, m. p. 242–248°, which gave no depression when mixed with an authentic sample, and, from the more soluble fraction, 36 mg. of another substance as colorless needles, m. p. 98–100°. After two recrystallizations this largely fused at 105.5–106.5°, but the melt became clear only at 165°. The trinitrobenzene derivative formed orange needles, m. p. 165–167°, from alcohol. The composition of the hydrocarbon is that of a methylchrysene.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.11; H, 5.88.

In another experiment 2.95 g. of the carbinol IX (R = CH₃) was dehydrated with potassium bisulfate at 180° and the oil (2 g.) treated at 0° with aluminum chloride in carbon bisulfide (nineteen hours). The material (1.35 g.) was then dehydrogenated and a crystalline trinitrobenzene derivative was separated and reconverted to the

(19) Sabatier and Mailhe, *Compt. rend.*, **140**, 841 (1905); von Auwers and Dersch, *J. prakt. Chem.*, **124**, 232 (1930).

hydrocarbon, giving 22 mg. of chrysene as the sole homogeneous product.

1 - (o - Chlorophenyl) - 2 - (α - naphthyl) - propene (X).—An ethereal solution of 3.2 g. of the aldehyde III was added at 0° to the reagent from 4.2 g. of o-chlorobromobenzene and 0.6 g. of magnesium and the temperature was slowly raised from 0° to the boiling point. The product was collected as a viscous oil (5.3 g.) which was heated with 7.5 g. of potassium bisulfate at 170–180° for one hour and distilled twice, giving a light yellow oil, b. p. 150–180° (1 mm.); yield 3.1 g. (64%).

Anal. Calcd. for C₁₉H₁₅Cl: C, 81.86; H, 5.42. Found: C, 81.27; H, 5.66.

In various experiments this olefin was refluxed with potassium hydroxide in quinoline for three hours, stirred with potassium hydroxide at 250–260° for seven minutes, or at 250–300° for twenty minutes, but this resulted only in tars or in oils from which no crystalline trinitrobenzene derivative could be isolated. The carbinol was also fused with potassium hydroxide under various conditions without successful result.

When o-bromoiodobenzene was used in the synthesis the distilled carbinol contained only 13.0% of halogen, as compared with the theoretical value of 23.4%. No satisfactory product was obtained on dehydration and alkali fusion.

Summary

A convenient method of preparing 2-(α-naph-
thyl)-propionaldehyde has been found in the condensation of α-naphthylmagnesium bromide with methoxyacetonitrile followed by a methyl Grignard reaction on the resulting methoxymethyl α-naphthyl ketone and acid dehydration of the carbinol. The aldehyde can be reduced smoothly to the alcohol and the latter converted into the chloride.

With these intermediates readily available, an attempt was first made to synthesize 5-methylchrysene by the Bogert–Cook method, but there was obtained instead a hydrocarbon identical with Newman's 6-methylchrysene. Apparently in analogy with the para migration of a methyl group attached to a saturated ring observed by Haworth, an ortho methyl migration occurs in the dehydrogenation.

Various other possible methods of utilizing the same intermediates for the synthesis of 5-methylchrysene were explored without success, the difficulty being associated in part with the ready loss of methyl from the 5-position, as observed by W. E. Jones and Ramage.

Converse Memorial Laboratory
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The Oxygen Effect in the Reaction of Cyclopropane with Bromine and with Hydrogen Bromide

By M. S. Kharasch, M. Z. Fineman and F. R. Mayo

Previous papers from this Laboratory[1-3] have shown that the brominations of toluene and phenanthrene are markedly accelerated by traces of oxygen and peroxides. These and similar observations with other hydrocarbons[4] have led us to reëxamine the reactions of cyclopropane with bromine and with hydrogen bromide.

Previous Work

The literature on the reaction of cyclopropane with bromine and hydrogen bromide is meager, although a great deal of work has been done with substituted cyclopropanes.[5] Gustavson[6] states

that at ordinary temperatures cyclopropane reacts with bromine quite slowly in the dark, and rapidly in sunlight. He noted that propyl bromide, more highly brominated products, and large quantities of hydrogen bromide were formed in addition to trimethylene bromide. Ogg and Priest[7] have investigated several vapor phase reactions of cyclopropane. At 250° iodine yielded 1,3-diiodopropane and light had no effect on the reaction. At room temperature under intense illumination, bromine added to give mostly 1,3-dibromopropane and a little hydrogen bromide. At 220° in the dark, large proportions of hydrogen bromide were formed. Hydrogen bromide gave little indication of reaction at 300°.

Experimental Part

The cyclopropane used in this work was obtained from the Ohio Chemical Company. It boiled at −33.5 to

(1) Kharasch, Margolis, White and Mayo, This Journal, 59, 1405 (1937).

(2) Kharasch, White and Mayo, J. Org. Chem., 2, 574 (1938).

(3) Kharasch, White and Mayo, ibid., 3, 33 (1938).

(4) Kharasch, Hered and Mayo, unpublished work.

(5) (a) Farmer, J. Chem. Soc., 123, 3341 (1923); (b) Demjanow and Dojarenko, Ber., 56B, 2200 (1923); (c) Nicolet and Sattler, This Journal, 49, 2066 (1927); (d) Bone and Perkin, J. Chem. Soc., 67, 118 (1895); (e) Gustavson, J. prakt. Chem., [2] 62, 270 (1900).

(6) Gustavson, ibid., [2] 62, 273 (1900).

(7) Ogg and Priest, This Journal, 60, 217 (1938).