aromatic, dibasic saturated and β-halogen. The reaction may be considered therefore as general.

The tertiary alcohols thus obtained can be transformed easily by dehydration into the corresponding olefins. In the case of 1,2-unsaturated acids, the tertiary alcohols obtained lose water easily, sometimes even during the preparation procedure, and pass into the respective cyclic olefins.

BUCHAREST, ROUMANIA RECEIVED JUNE 30, 1948[6]

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[6] Publication delayed because of difficulty of communication.

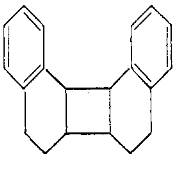
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, SCOALA POLITEHNICA]

The Polymerization of 1,2-Dihydronaphthalene and the Dehydrogenating Condensation of 1,2,3,4-Tetrahydronaphthalene

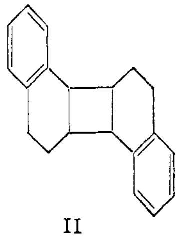
BY COSTIN D. NENITZESCU AND MARGARET AVRAM

By the action of sulfuric acid on 1,2-dihydronaphthalene (dialin), von Braun and Kirschbaum[1] obtained a solid dimeride $C_{20}H_{20}$ (m. p. 93°), which they called bis-dialin, along with a liquid isomeride corresponding to the same empirical formula but probably not of uniform composition. To these hydrocarbons, which possess a saturated character, the structures I or II have been attributed.

These hydrocarbons, dehydrogenated with lead oxide, yield a yellow hydrocarbon $C_{20}H_{12}$ (m. p. 165°) named by the above authors bis-naphthylene. To these, similar formulas have been assigned with all the four cycles being aromatic.



I



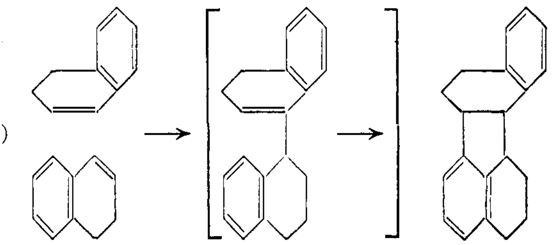
II

By the action of aluminum chloride on tetralin, at 30–80°, Dansi and Ferri[2] obtained a hydrocarbon $C_{20}H_{20}$ (m. p. 150.5°), which by dehydrogenation with selenium, yields a hydrocarbon, thoroughly aromatic in character, $C_{20}H_{12}$ (m. p. 165°), which yields a picrate of m. p. 195°.

By repeating the experiments of von Braun and Kirschbaum we found that their hydrocarbon $C_{20}H_{12}$ gives a picrate which melts at the same temperature as that indicated by Dansi and Ferri. Thus, it is obvious that the hydrocarbons $C_{20}H_{12}$, obtained by these authors, are identical. We were unable to reproduce the work of Dansi and Ferri, probably because we had no precise knowledge of the conditions under which this work was accomplished. The results which we obtained by treating tetralin with aluminum chloride, under various conditions, coincide exactly with those described by G. Schroeter.[3]

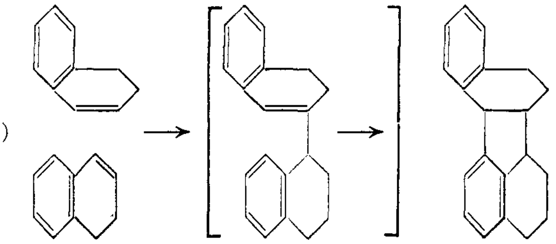
Working Hypothesis.—The structures I and II, with their cyclobutanic cycles, seem improbable; therefore we propose for the dimerization of 1,2-dialin under the influence of sulfuric acid, one of the following two mechanisms.

(A)



III

(B)



IV

The transformation which the tetralin molecule undergoes through the influence of aluminum chloride, in the reaction of Dansi and Ferri, is a dimerization with elimination of hydrogen.

$$2C_{10}H_{12} \longrightarrow C_{20}H_{20} + 4[H]$$

The expelled hydrogen is used in undefined hydrogenation reactions. The probable course of this reaction is as follows: first, a molecule of tetralin loses two hydrogen atoms, passing into 1,2-dialin. Such formation of an olefin from a saturated hydrocarbon, under the influence of aluminum chloride, has been proved in other instances.[4] The resulting dialin reacts then with tetralin, which is present in great excess, following one of the mechanisms shown.

If these hypotheses are correct, the two isomeric hydrocarbons, $C_{20}H_{20}$ (m. p. 93 and 150.5°), ought to possess the structure III and IV, respectively. The hydrocarbon $C_{20}H_{12}$ with the

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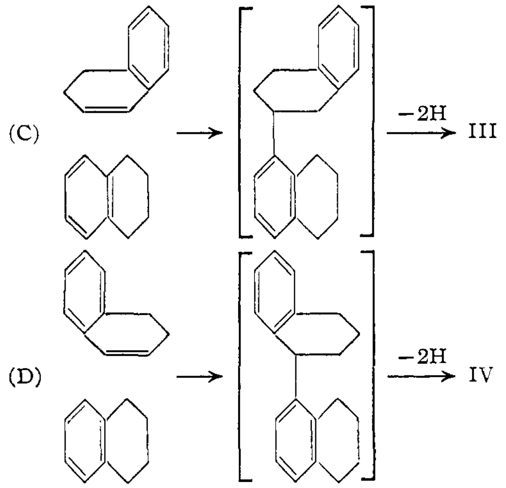
(1) Julius von Braun and G. Kirschbaum, *Ber.*, **54**, 597 (1921).

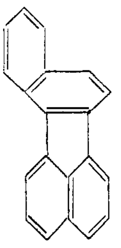
(2) A. Dansi and G. Ferri, *Gazz. chim. ital.*, **71**, 648 (1941); *Chem. Centr.*, **113**, I, 2525 (1942).

(3) G. Schroeter, *Ber.*, **57**, 1990 (1924).

(4) C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **419**, 189 (1931).

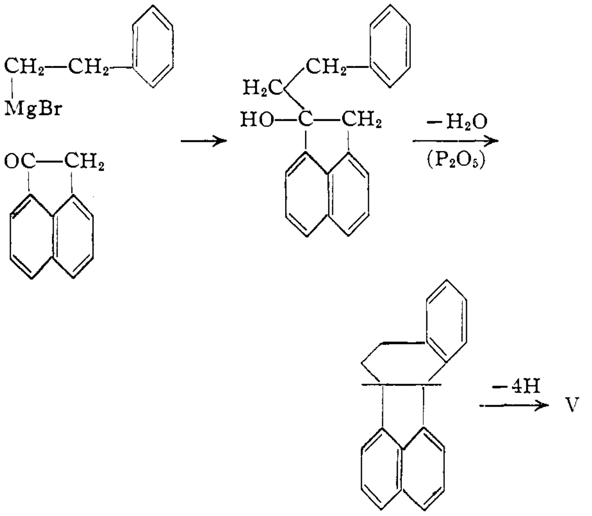


m. p. 165°, which is formed by the dehydrogenation of both these hydrocarbons, should be therefore 10,11-benzofluoranthrene (V).



V

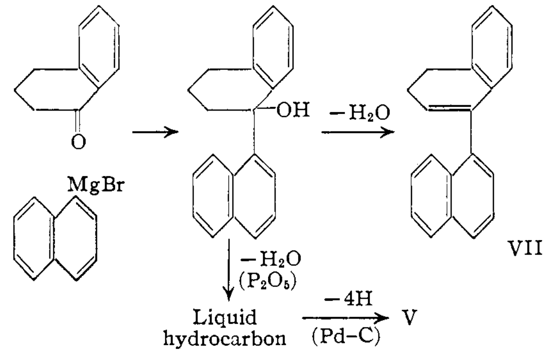
Syntheses of 10,11-Benzofluoranthrene.—In order to check the hypotheses indicated above, the hydrocarbon (V) was first synthesized as shown in the formulas



VI

By the addition of phenylethylmagnesium bromide to acenaphthenone, a non-crystallizing tertiary alcohol was obtained. Distilled under reduced pressure it easily eliminates water, passing into an unsaturated hydrocarbon. As the cyclization of this hydrocarbon was not successful the direct cyclodehydration of the raw tertiary alcohol, with phosphorus pentoxide,[5] at 145°, was tried. Thus an aromatic colorless, crystalline hydrocarbon with m. p. 163° was obtained, the elementary analysis of which indicated the formula $C_{20}H_{16}$ and which therefore is 9,12,13,14-tetrahydro-10,11-benzofluoranthrene (VI). By dehydrogenation of this hydrocarbon with palladium–charcoal a yellow hydrocarbon (m. p. 165°) of the formula $C_{20}H_{12}$ was formed, which therefore is the 10,11-benzofluoranthrene. The mixed melting point with bis-naphthylene prepared according to von Braun and Kirschbaum gave no depression; the same happens with the melting points of the corresponding picrates.

Another synthesis of benzofluoranthrene (V) has been achieved by the following procedure, starting with 1-naphthylmagnesium bromide and 1-tetralone



As in the preceding case, the tertiary alcohol did not crystallize. By distillation *in vacuo*, water was eliminated easily and an unsaturated hydrocarbon, $C_{20}H_{16}$ (m. p. 120.5°), was obtained, which is 3,4-dihydro-1,1′-binaphthyl (VII). The attempted cyclization of this hydrocarbon, which was tried with sulfuric acid, aluminum chloride, stannic chloride and phosphorus pentoxide, did not succeed; this confirms similar facts observed with 1-naphthylcyclohexane.[6] The tertiary alcohol, when treated with phosphorus pentoxide at 120–140° yields however a liquid hydrocarbon, which did not crystallize even after distillation, but which passed into 10,11-benzofluoranthrene, when dehydrogenated with palladium–charcoal. The identity of the product has been checked as above.

A third synthesis of the hydrocarbon V has been effected starting from 5-iodo-1,2,3,4-tetralin, prepared by diazotization of 5-amino-1,2,3,4-tetralin.

It was not possible to obtain the tertiary alcohol in the crystallized state; neither was this possible for the hydrocarbon resulting from the dehydration of the former with phosphorus pentoxide. It is noticeable that, by the dehydration of the tertiary alcohol with phosphorus pentoxide, hydrogen is eliminated from the saturated cycle

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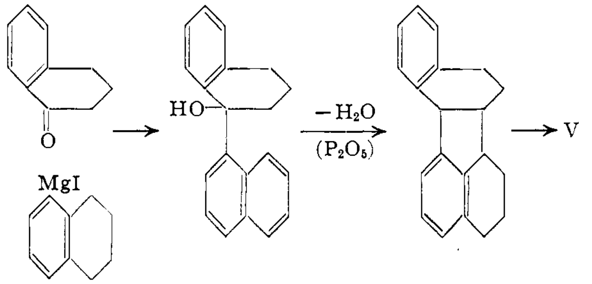
[5] C. D. Nenitzescu, E. Cioränescu and M. Maican, *Ber.*, **74**, 687 (1941).

[6] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1431 (1936).

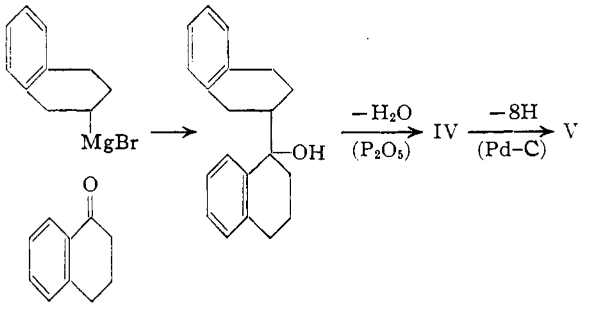


of the tetralin residue. By dehydrogenating the liquid hydrocarbon with palladium charcoal 10,11-benzofluoranthrene was obtained in good yield.

Synthesis of the Hydrocarbon $C_{20}H_{20}$ of M. p. 150.5°.—In order to check the reaction mechanism expressed by the equation C or D shown above, the condensation of 1,2-dialin with tetralin was tried. This reaction did not succeed with aluminum chloride, but with phosphorus pentoxide a hydrocarbon, $C_{20}H_{20}$ of m. p. 150.5°, was obtained which, without doubt, is identical with the one described by Dansi and Ferri. The dehydrogenation of this compound with palladized charcoal yields 10,11-benzofluoranthrene of m. p. 165° and the corresponding picrate of m. p. 195°.

The hydrocarbon $C_{20}H_{20}$ (m. p. 150.5°) is also formed by hydrogenating 10,11-benzofluoranthrene with sodium and isoamyl alcohol.

Neither of these reactions permits a choice between the two possible structures III and IV for the hydrocarbon with the m. p. 150.5°, but this point was decided finally by the following method.

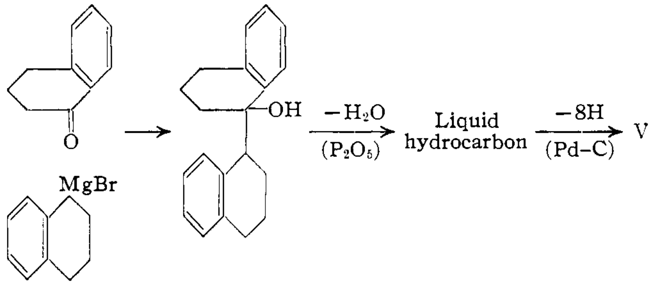


For the preparation of the 2-bromo-1,2,3,4-tetralin, necessary for this reaction, we started from 2-tetralol, obtained from 2-naphthol by hydrogenation with a copper–chromoxide catalyst, according to Adkins and Musser.[7] By the action of phosphorus tribromide the 2-tetralol was transformed into the 2-bromo derivative, a very unstable product which eliminated hydrobromic acid easily and which therefore could not be separated in a pure state. Nevertheless, the preparation of the Grignard derivative succeeded well, starting with the raw reaction product.

By the cyclodehydration, with phosphorus pentoxide, of the tertiary alcohol, we obtained an oil which in four days deposited crystals corresponding to the formula $C_{20}H_{20}$ having a m. p. 150.5°. This substance does not show a depression of the melting point with the hydrocarbon obtained by the condensation of dialin with tetralin. By dehydrogenation it yields 10,11-benzofluoranthrene.

This reaction shows that the hydrocarbon $C_{20}H_{20}$ with m. p. 150.5° has the structure IV and therefore is 1,2,3,4,9,12,13,14-octahydro-10,11-benzofluoranthrene. Thus, it is likely that this hydrocarbon is formed by the catalytic action of aluminum chloride on tetralin, according to scheme D.

The Structure of the Hydrocarbon $C_{20}H_{20}$ of M. p. 93°.—Having established that the hydrocarbon of m. p. 150.5° possesses the structure IV, the probability is great for the isomeride of m. p. 93° to correspond to the structure III. In order to prove the structure of this compound the Grignard derivative of 1-bromotetralin was condensed with 1-tetralone



As in the case of the other isomeride, the 1-bromotetralin loses, during distillation under reduced pressure, a part of its bromine content and therefore the raw reaction product was utilized. By the cyclodehydration of the tertiary alcohol with phosphorus pentoxide we obtained a liquid hydrocarbon, which after some days deposits colorless crystals with m. p. 83°, corresponding to the formula $C_{20}H_{22}$. These crystals have been proved to be 1,1′-ditetralyl, resulting from a Wurtz reaction between two molecules of 1-bromotetralin. By the dehydrogenation of the former with palladium–charcoal we obtained the 1,1′-binaphthyl of m. p. 157°.

The oil which remained after the filtration of the said crystals does not crystallize after six weeks. But by the dehydrogenation with palladium-charcoal it yields 10,11-benzofluoranthrene, identified by its melting point and mixed melting point as well as by the m. p. of its picrate. It is thus likely that this oil contains a certain amount of the hydrocarbon $C_{20}H_{20}$ of the m. p. 93°, whose tendency to crystallize is smaller.

The structure of this product is probably that shown by formula III, 5,6,7,8,9,12,13,14-octahydrobenzofluoranthrene. This compound is

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[7] H. Adkins and D. M. Musser, THIS JOURNAL, **60**, 664 (1938).

thus formed by the polymerization of dialin, under the action of sulfuric acid,[1] corresponding to scheme A.

In the literature there is only one indication which pleads against the structures proposed above. According to von Braun and Kirschbaum[1] the dehydrogenation of 2,2′-ditetralyl with sulfur, at 205°, yields "bis-naphthylene," $C_{20}H_{12}$, but only in an impure condition, m. p. 158–160°. As the formation of 10,11-benzofluoranthrene by this method seemed unlikely, the 2,2′-ditetralyl was prepared following von Braun and Kirschbaum and then was dehydrogenated with sulfur, according to the directions of those authors, as well as with palladium–charcoal. In both cases only 2,2′-binaphthyl[8] was obtained with good yields (m. p. 187°). The compound has been identified by the mixed melting point with a standard sample.

Experimental

10,11-Benzofluoranthrene from Phenylethylmagnesium Bromide and Acenaphthenone.—A Grignard derivative was prepared in the usual way from 15 g. of phenylethyl bromide and 2 g. of magnesium in 120 cc. of ether. A solution of 8 g. of acenaphthenone in 20 cc. of benzene and 80 cc. of ether was then added in the cold. After heating for an hour, the mixture was decomposed by a saturated solution of ammonium chloride. After evaporation of the ether and an hour of drying on the steam-bath at reduced pressure, 10 g. (40%) of the raw tertiary alcohol was obtained. This was mixed thoroughly with 30 g. of phosphorus pentoxide and heated an hour at 140° (thermometer inside the flask). After cooling, water was added, the oil dissolved in benzene, the solvent evaporated and the compound finally dried *in vacuo*. After twelve hours of waiting, some colorless crystals appeared, which recrystallized first from ethanol then from methanol, showed the m. p. 163° of 9,12,13,14-tetrahydro-10,11-benzofluoranthrene. The yield was 4 g. (44%).

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.28. Found: C, 93.52; H, 6.61.

0.30 g. of the tetrahydrobenzofluoranthrene was heated with 0.15 g. of palladium–charcoal (27%) in a nitrogen atmosphere for one hour at 330°. The substance was extracted with benzene and recrystallized from ethanol; yellow needles, m. p. 165°. The yield was nearly quantitative.

Anal. Calcd. for $C_{20}H_{12}$: C, 95.21; H, 4.79. Found: C, 95.11; H, 5.03.

The mixed melting point with "bis-naphthylene" showed no depression. The picrate, brick red in color, has been prepared in ethanol solution; m. p. 195°; mixed m. p. of the picrate obtained from "bis-naphthylene" gave no depression.

10,11-Benzofluoranthrene from 1-Naphthylmagnesium Bromide and 1-Tetralone.—To the Grignard derivative prepared from 15 g. of 1-bromonaphthalene and 1.1 g. of magnesium in 120 cc. of ether, 8.8 g. of 1-tetralone dissolved in 70 cc. of ether was added, drop by drop. After the usual procedure, the crude tertiary alcohol obtained (9 g.) was heated *in vacuo* on a steam-bath for an hour. Fifteen grams of phosphorus pentoxide was added to the mixture, which was then heated for an hour at 140°. After decomposing it with water, extraction with benzene and washing with water, the benzene was evaporated and the product distilled under reduced pressure. The fraction which passed in the range of 200–240° at 10 mm. (3 g.) was left for six weeks in a vacuum desiccator; but even after this lapse of time it did not crystallize. The dehydrogenation of this oil with palladium–charcoal in the manner described above, gave a yellow crystalline product of m. p. 165°, soaked with some oil. The identification as 10,11-benzofluoranthrene was done as shown above.

In another experiment the raw tertiary alcohol, obtained by decomposing the Grignard derivative, was distilled under reduced pressure. The fraction from 230–250° at 10 mm. forms into a glassy mass, which deposits colorless crystals of m. p. 120.5° (from methanol), being 3,4-dihydro-1,1′-binaphthyl; yield 8.5 g. (20%).

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.28. Found: C, 93.87; H, 6.35.

The substance decolors bromine water and alkaline permanganate solution.

10,11-Benzofluoranthrene from 5-Iodotetralin and 1-Tetralone.—Fourteen grams of 5-aminotetralin[9] was poured into a cold mixture of 60 cc. of sulfuric acid and 60 cc. of water. The mixture deposes the difficultly soluble sulfate of the amine. Then 30 g. of crushed ice was added and while vigorously shaking the mixture, a saturated solution of 7 g. of sodium nitrite was dropped into it keeping the temperature between 0–3°. After filtration a saturated solution of 37 g. of potassium iodide and 12 g. of powdered copper, slightly wetted were added. The whole mixture was allowed to stand for two hours at ordinary temperature and was then heated for fifteen minutes on the steam-bath. The 5-iodotetralin formed by this procedure was vacuum distilled; b. p. 150–151° at 10 mm.; yield 10 g. (40%). The magnesium derivative, thus obtained from 10 g. of 5-iodotetralin, 0.9 g. of magnesium and 100 cc. of ether was treated in the cold with 5 g. of 1-tetralone. The tertiary alcohol, after being dried *in vacuo*, was heated for an hour with 15 g. of phosphorus pentoxide at 120–125° and distilled under reduced pressure. The fraction of b. p. 220–240° at 2 mm. was dehydrogenated with palladium–charcoal as shown above. 10,11-Benzofluoranthrene was formed, which was identified by its mixed melting point and picrate with the "bis-naphthylene" of von Braun and Kirschbaum.

The fraction of b. p. 240–260° at 2 mm., after being left to stand a few days, deposits yellow crystals of 10,11-benzofluoranthrene (m. p. 165°). Thus, a partial dehydrogenation takes place during the heating with phosphorus pentoxide.

The Preparation of the Hydrocarbon $C_{20}H_{20}$ of M. p. 150.5° from Tetralin and Dialin.—In a flask, provided with a thermometer and calcium chloride tube, 20 g. of phosphorus pentoxide, 15 g. of tetralin and 5 g. of 1,2-dialin (prepared according to von Braun and Kirschbaum[1]) were mixed and heated an hour at 140°. After washing with water and extraction with benzene, 2 g. of oil was obtained by distillation under reduced pressure (b. p. 225–226° at 10 mm.), which after some five days deposits crystals; m. p. from ethanol 150.5°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.54; H, 8.07.

By dehydrogenation with palladium–charcoal 10,11-benzofluoranthrene was obtained, identified by melting point, mixed melting point and picrate.

The Preparation of the Hydrocarbon $C_{20}H_{20}$ with M. p. 150.5° by the Hydrogenation of 10,11-Benzofluoranthrene.—Five grams of 10,11-benzofluoranthrene was refluxed with 200 cc. of isoamyl alcohol and then treated with 30 g. of metallic sodium in small amounts. The discolored solution was washed with water, the isoamyl alcohol removed by distillation under reduced pressure and the remaining oil kept for two months in vacuum, when it separates crystals which were dried on a porous plate and recrystallized from ethanol, m. p. 150.5°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.99; H, 7.68.

The mixed m. p. with the hydrocarbon obtained in the preceding experiment shows no depression.

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(8) J. Loevenich and A. Loeser, *Ber.*, **60**, 325 (1927).

(9) Prepared by the hydrogenation of 1-naphthylamine with sodium and isoamyl alcohol according to E. Bamberger and M. Althausse, *Ber.*, **21**, 1789 (1888).

1,2,3,4,9,12,13,14-Octahydro-10,11-benzofluoranthrene.—Eighteen grams of phosphorus tribromide diluted with 10 cc. of dry benzene were dropped into an ice-cooled solution of 20 g. of 2-tetralol[7] in 5 cc. of benzene. The product was left for six hours at room temperature, washed with ice-cooled water and a sodium bicarbonate solution, then it was diluted with 50 cc. of dry ether and dried a day long on sodium sulfate. When distillation under reduced pressure was attempted, a product distilled with b. p. 130–150° at 10 mm., which showed a bromine content of 14% instead of 37.9%, proving decomposition with elimination of hydrobromic acid.

The ether–benzene solution of 2-bromotetralin, prepared as indicated above, was treated with 2 g. of magnesium and 250 cc. of dry ether in the usual manner and after complete dissolution was treated with a mixture of 8 g. of 1-tetralone in 80 cc. of ether. After the usual procedure, the solvent was removed and the remaining product was steam distilled. The residual oil was extracted with benzene, the solution dried and the benzene was removed. The residue (10 g.) was heated with 15 g. of phosphorus pentoxide at 130–140°. After washing with water and extraction with benzene, an oil was obtained whose main part (4–5 g.) distilled in the range of 195–197° at 1 mm. After ten days the distillate deposited colorless needles which recrystallized from ethanol showed the m. p. 150.5°. The mixed melting point with the hydrocarbon obtained by the procedures described above did not give any depression.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.57; H, 8.49.

By the dehydrogenation with palladium–charcoal 10,11-benzofluoranthrene was obtained in yellow needles, melting at 165°; the picrate melts at 195°.

Attempted Synthesis of the Hydrocarbon $C_{20}H_{20}$ with M. p. 93°.—Starting with 1-tetralole,[7] 1-bromotetralin was prepared, which was transformed into the corresponding magnesium derivative and treated with 1-tetralone, in a manner quite similar to that described above. The oil obtained after treatment with phosphorus pentoxide gave the b. p. 203–204° at 2 mm. After one day it deposits a small amount of colorless crystals referred to later. The oil left after the filtration of these crystals did not crystallize any more during the following six weeks. By dehydrogenation with palladium–charcoal it gave, in good yield, 10,11-benzofluoranthrene, identified by m. p., mixed m. p. and picrate.

1,1'-Ditetralyl.—The crystals obtained above as a secondary reaction product, after being recrystallized from ethanol, showed the m. p. 83°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.54; H, 8.45. Found: C, 91.30; H, 8.70.

By dehydrogenation for an hour with palladium–charcoal in an atmosphere of carbon dioxide, colorless crystals of m. p. 157° were obtained. The mixed melting point with 1,1'-bis-naphthyl,[10] gave no depression.

Summary

1 It has been shown, by synthesis, that the hydrocarbon $C_{20}H_{20}$ with m. p. 150.5°, which was obtained by Dansi and Ferri[2] by the action of aluminum chloride on 1,2,3,4-tetralin, is 1,2,3,4-9,12,13,14-octahydro-10,11-benzofluoranthrene.

2. The hydrocarbon $C_{20}H_{20}$ with m. p. 93°, obtained by von Braun and Kirschbaum[1] by the polymerization of 1,2-dialin with sulfuric acid is very probably 5,6,7,8,9,12,13,14-octahydrobenzofluoranthrene.

3. It has been shown by six different syntheses that the hydrocarbon $C_{20}H_{12}$ which is formed by the dehydrogenation of the preceding hydrocarbons, is 10,11-benzofluoranthrene.

BUCHAREST, ROUMANIA RECEIVED JUNE 30, 1948[11]

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[10] Prepared according to E. Sakellarios and Th. Kyrmis, *Ber.*, **57**, 324 (1924).

[11] Delayed because of difficulty of communication.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

The Molecular Structure of N-Methylacetamide

BY SAN-ICHIRO MIZUSHIMA, TAKEHIKO SIMANOUTI, SABURO NAGAKURA, KENJI KURATANI, MASAMICHI TSUBOI, HIROAKI BABA AND OSAMU FUJIOKA

In the present paper we report the experimental results of the Raman effect, infrared absorption, ultraviolet absorption and dipole moment observed for N-methylacetamide, $CH_3CONHCH_3$, which is the simplest molecule containing the peptide bond and hence can be regarded as a structural unit of the polypeptide chain. A sample prepared by Dr. Kanji Mayumi and Ichiro Okano was subjected several times to vacuum distillation and was used in this experiment (m. p. 28°).

Raman Effect and Infrared Absorption in the Rock Salt Region

The experimental results of the Raman effect and infrared absorption for the liquid at ordinary temperature are shown in Table I.[1] As to the Raman effect the measurement was also made for the liquid at 90–95°, for the aqueous solution (pH = 4), and for the acidic solution (hydrochloric acid, pH = 1). The result obtained was essentially the same as in the case for the liquid at ordinary temperature. We can, therefore, consider that N-methylacetamide consists of only one kind of molecule, otherwise the spectrum would change at higher temperature or in solutions.

The skeleton of this molecule consists of five atoms (C, O and N atoms) and, therefore, the skeletal frequencies number $3 \times 5 - 6 = 9$. As shown in Table I, we have observed almost the expected number of skeletal frequencies and we thus have another reason to believe that there is only one kind of molecule. The normal vibration calculation[2] which would take too much space

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[1] As to the previous measurement in the liquid state see: Kohlrausch and Seka, *Z. physik. Chem.*, **B43**, 355 (1939).

[2] The details will be published elsewhere: see also Simanouti, *J. Chem. Phys.*, **17**, 245, 848 (1949).