Further elution with benzene gave an intermediate fraction (0.6 g.) and then 0.80 g. (20%) of presumed XXIII, m.p. *ca.* 150–178°, which upon recrystallization from benzene gave 0.68 g. (17%; m.p. 178.5–184°) and finally colorless XXIII with a constant m.p. 183.5–184.5°; reported,[42] 174.5°.

Anal. Calcd. for $C_{13}H_8N_2O_5S_2$: C, 46.42; H, 2.40; S, 19.07. Found: C, 46.79; H, 2.69; S, 19.00.

Elution with ethyl acetate gave only gum (0.7 g.) and 0.13 g. of a solid (m.p. 160–173°, different from XXIII).

Acknowledgment. The authors are indebted to the Office of Ordnance Research, U. S. Army, for generous financial support of this investigation.

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(42) W. R. Waldron and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 2403 (1923).

[CONTRIBUTION FROM THE RADIUM INSTITUTE OF THE UNIVERSITY OF PARIS]

Orientation in Friedel-Crafts Acylations of 6-Substituted Chrysenes

PHILIPPE MABILLE AND N. P. BUU-HOÏ

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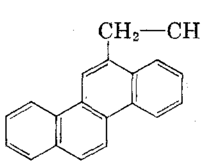
The Friedel-Crafts acylations of 6-ethyl- and 6-benzylchrysene are shown to take place in position 12; in the case of 6-benzylchrysene and acetyl chloride some disubstitution occurs, to give a diketone whose constitution is shown to be 6-(4′-acetylbenzyl)-12-acetylchrysene.

Whereas there is abundant proof[1] that Friedel-Crafts reactions with chrysene occur preferentially in position 6, the orientation in similar substitution reactions with 6-alkylchrysenes has hitherto not been investigated. In theory, such reactions should lead to 12-substituted derivatives, the positions 6 and 12 in the molecule of chrysene being the most reactive sites in view of their high free valence index.[2] Furthermore, we recently established that 6-ethylchrysene undergoes nitration to give 6-ethyl-12-nitrochrysene.[3]

The present work records the results of Friedel-Crafts acylations of 6-ethylchrysene (I) and 6-benzylchrysene (II). The aluminum chloride-catalyzed reaction of benzoyl chloride with (I), using carbon disulfide as the solvent, had been studied by Funke and Ristic,[4] who obtained a monoketone whose structure they did not investigate. We now found that this ketone readily underwent Wolff-Kishner reduction to give a 6-ethyl-x-benzylchrysene. The same hydrocarbon was obtained when 6-benzylchrysene was submitted to acetylation with acetyl chloride and aluminum chloride and the resulting ketone reduced by the Wolff-Kishner method. The fact that the same hydrocarbon was obtained in these two sets of reactions shows that it was 6-ethyl-12-benzylchrysene (IV), the starting ketones therefore being, respectively, 6-ethyl-12-benzoylchrysene (III) and 6-benzyl-12-acetylchrysene (V). These experimental results confirm those obtained by π-electron density computations as regards the pronounced reactivity of both positions 6 and 12 in the molecule of chrysene.



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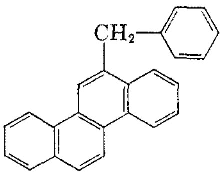

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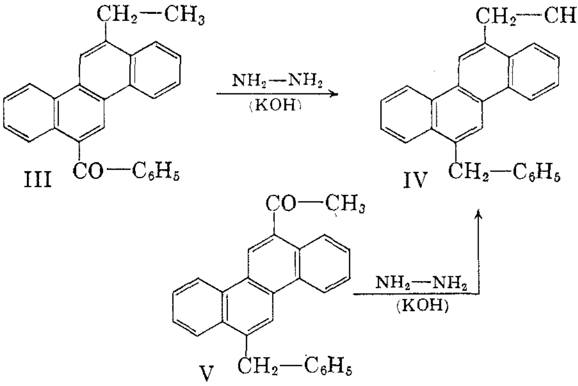

It is of interest to note that in the Friedel-Crafts acetylation of 6-benzylchrysene, small amounts of a diketone were obtained along with the monoketone (V). This by-product was found to be 6-(4′-acetylbenzyl)-12-acetylchrysene (VI), as it underwent Wolff-Kishner reduction to a hydrocarbon, which could also be prepared in a different way, *viz.* Friedel-Crafts acylation of 6-ethylchrysene with *p*-ethylbenzoyl chloride followed by reduction of the ensuing ketone, which therefore must have been 6-ethyl-12-(4′-ethylbenzoyl) chrysene (VII). Hence, the hydrocarbon in ques-

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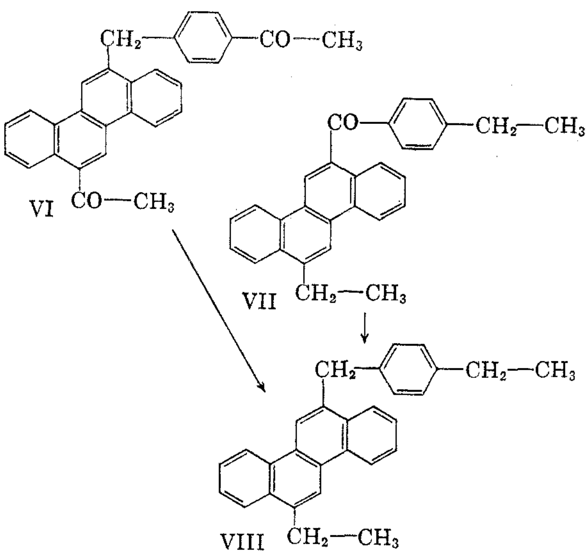
(1) See, for instance, F. Bergmann and H. E. Eschinazi, *J. Am. Chem. Soc.*, **65**, 1413 (1943); N.P. Buu-Hoï, *J. Org. Chem.*, **19**, 721 (1954).

(2) *Dictionary of Values of Molecular Constants (calculated theoretically by Wave Mechanical Methods)*, Vol. II, p. 29 (C. A. Coulson and R. Daudel, eds., Oxford and Paris).

(3) P. Mabille and N. P. Buu-Hoï, *J. Org. Chem.*, **25**, 216 (1960).

(4) K. Funke and J. Ristic, *J. prakt. Chem.*, [2] **146**, 151 (1936).

tion was 6-ethyl-12-(4′-ethylbenzyl)chrysene (VIII).



In the Friedel-Crafts benzoylation of chrysene, the main product obtained was 6-benzoylchrysene,[5] but two isomeric benzoylchrysenes were also formed in very small amounts. Because of the poor yields of these isomers, no structure determinations could be made, but, by analogy with Carruthers' findings in respect to the acetylation of chrysene[6] (he obtained small quantities of 2- and 3-acetylchrysene along with the 6-isomer), the two new benzoylchrysenes were most likely 2- and 3-benzoylchrysene.

EXPERIMENTAL

Benzoylation of chrysene. The following procedure was an improvement on the method described by Funke and Müller[5] for the preparation of 6-benzoylchrysene. To a suspension of 22.8 g. of pure chrysene in 1000 ml. of dry carbon disulfide containing 20 ml. of benzoyl chloride, 16 g. of finely-powdered aluminum chloride was added in small portions with stirring, during 10 min.; the mixture was left for 14 hr. at room temperature, then refluxed for 4 hr. After decomposition with ice and hydrochloric acid, and addition of *ca.* 1000 ml. of methylene chloride, the organic layer was washed with water and filtered. Evaporation of the solvents left a brownish semicrystalline mass, which was washed several times with hot water in order to dissolve the benzoic acid; this residue was recrystallized first from toluene, then from benzene-ethanol, to furnish 22.5 g. (62% yield) of *6-benzoylchrysene,* shiny cream-colored leaflets, m.p. 192° (lit.,[5] m.p. 191°), giving a blood red coloration in sulfuric acid.

Concentration of the mother liquors from the second crystallization yielded 5 g. of leaflets, m.p. 185–190°. Fractional crystallization of this portion from toluene afforded 2 to 3 g. of 6-benzoylchrysene, along with 0.1 to 0.2 g. of *x-benzoylchrysene,* which crystallized from acetic acid in almost colorless needles, m.p. 256° (sublimation above 240°), whose solutions in sulfuric acid were deep red, rapidly turning orange-brown.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.3; H, 4.9; O, 4.8. Found: C, 90.1; H, 5.0; O, 5.0.

The residue from evaporation of the first mother liquors was submitted to fractional recrystallization, first from acetone, then from acetic acid, to give 0.1 g. of *y-benzoylchrysene,* cream-colored leaflets, m.p. 224°, whose solutions in sulfuric acid were brown-yellow.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.3; H, 4.9. Found: C, 90.2; H, 4.7.

Preparation of 6-benzylchrysene (II). Reduction of 6-benzoylchrysene was effected more conveniently by the Wolff-Kishner than by the Clemmensen method.[5] A mixture of 9 g. of 6-benzoylchrysene, 9 g. of 98% hydrazine hydrate, and 350 ml. of diethylene glycol was refluxed for 7 hr. with 9 g. of potassium hydroxide; after cooling, dilute hydrochloric acid was added, and the precipitate was recrystallized from acetone, giving 5.2 g. (61% yield) of long colorless needles, m.p. 202–203°; lit.,[5] m.p. 200°.

Benzoylation of 6-ethylchrysene. 6-Ethylchrysene was prepared according to the literature.[3] To a solution of 5 g. of 6-ethylchrysene and 7.5 ml. of benzoyl chloride in 100 ml. of carbon disulfide, 5 g. of aluminum chloride was added with stirring, during 15 min. The mixture was left for 14 hr. at room temperature, then refluxed for 2 hr., and worked up as in the case of chrysene. The reaction product was crystallized, first from ethanol, then from ethanol-acetone, to yield 3.6 g. (50%) of *6-ethyl-12-benzoylchrysene* (III), fine yellow needles, which melted at 134°, then resolidified, to melt anew at 147–149° (lit.,[4] m.p. 130°); the coloration in sulfuric acid was cherry red.

Anal. Calcd. for $C_{27}H_{20}O$: C, 90.0; H, 5.6. Found: C, 89.8; H, 5.6.

6-Ethyl-12-benzylchrysene (IV). Reduction of 1.3 g. of the foregoing ketone was effected with 1.3 g. of hydrazine hydrate and 1.3 g. of potassium hydroxide in 50 ml. of diethylene glycol in the usual way. The yield was 0.8 g. of a *hydrocarbon,* crystallizing from ethanol-acetone in silky colorless needles, m.p. 169–170°.

Anal. Calcd. for $C_{27}H_{22}$: C, 93.6; H, 6.4. Found: C, 93.7; H, 6.4.

Acetylation of 6-benzylchrysene. To a solution of 15 g. of 6-benzylchrysene and 60 ml. of acetyl chloride in 600 ml. of carbon disulfide, 15 g. of aluminum chloride was added in small portions with stirring, during 20 min., and the mixture then treated as above. After decomposition with ice and hydrochloric acid, the solvent was distilled, and the residual brown crystalline mass (19 g.) was extracted with cyclohexane (2000 ml.). Concentration of the cyclohexane solution to 50 ml. yielded a precipitate which was recrystallized from ethanol, giving *6-benzyl-12-acetylchrysene* (V) (0.5 g.), pale yellow needles, m.p. 164–165°, whose solutions in sulfuric acid were orange-yellow.

Anal. Calcd. for $C_{27}H_{20}O$· C, 90.0; H, 5.6. Found: C, 89.9; H, 5.6.

The residue from the extraction with cyclohexane was taken up in acetone; evaporation of the acetone left a compound which was recrystallized several times from benzene and from benzene-acetone, to give *6-(4′-acetylbenzyl)-12-acetylchrysene* (VI) (4 g.), cream-colored needles, m.p. 226–227°, whose solutions in sulfuric acid were orange-yellow.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.5; H, 5.5; O, 8.0. Found: C, 86.3; H, 5.5; O, 8.0.

Reduction of 6-benzyl-12-acetylchrysene. Wolff-Kishner reduction of 0.3 g. of this ketone was effected in the usual way, giving a hydrocarbon (0.1 g.) which crystallized first from ethanol, then from acetone, in colorless needles, m.p. 169–170°, identical with compound IV (no depression in mixed melting point).

Reduction of 6-(4′-acetylbenzyl)-12-acetylchrysene. This reduction, performed with 0.8 g. of the diketone (VI), yielded *6-ethyl-12-(4′-ethylbenzyl)chrysene* (VIII), crystallizing from ethanol-acetone in silky colorless needles (0.6 g.), m.p. 179–180°.

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[5] K. Funke and E. Müller, *J. prakt. Chem.,* [2] **144,** 242 (1936).

[6] W. Carruthers, *J. Chem. Soc.,* 3486 (1953).

Anal. Calcd. for $C_{29}H_{26}$: C, 93.0; H, 7.0. Found: C, 93.2; H, 6.8.

6-Ethyl-12-(4'-ethylbenzoyl)chrysene (VII). To a solution of 5.2 g. of 6-ethylchrysene and 5 g. of *p*-ethylbenzoyl chloride in 80 ml. of carbon disulfide, 4.5 g. of aluminum chloride was added, and the mixture treated in the usual way. The resinous mass obtained was taken up in cyclohexane, and concentration of the cyclohexane solution yielded crystals, which were recrystallized from ethanol-acetone to give 4.4 g. (56%) of colorless leaflets, m.p. 113–114°, whose solutions in sulfuric acid were raspberry red.

Anal. Calcd. for $C_{29}H_{24}O$: C, 89.7; H, 6.2; O, 4.1. Found: C, 89.6; H, 6.2; O, 4.4.

Wolff-Kishner reduction of this ketone (1.7 g.) afforded a hydrocarbon (1.2 g.), m.p. 179–180°, identical with compound VIII.

Acknowledgment. This work was conducted with the financial aid of The Anna Fuller Fund, New Haven, Conn.; the authors express their gratitude to Professor William U. Gardner and the Trustees of the Fund.

PARIS (VE) FRANCE

[CONTRIBUTION FROM THE RADIUM INSTITUTE OF THE UNIVERSITY OF PARIS]

The Elbs Reaction of 6-(*o*-Toluoyl)chrysene and Similar Ketones

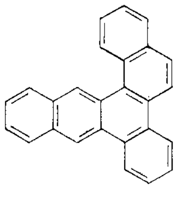
PHILIPPE MABILLE AND N. P. BUU-HOÏ

Received January 19, 1960

The Elbs reaction of 6-(*o*-toluoyl)chrysene has been investigated, and found to give rise predominantly to 15-oxatribenzo [a,e,jk]pyrene, with small amounts of benzo[a]naphtho[1,2-a]anthracene; similar compounds were obtained from the pyrolysis of 6-(2,4-dimethylbenzoyl)chrysene.

In view of the pronounced carcinogenic activity of many hexacyclic aromatic hydrocarbons,[1] a systematic investigation of other members of that group is being undertaken in this laboratory. Benzo[a]naphtho[1,2-a]anthracene (I), a hexacyclic derivative of chrysene, was included in this research, and a method for its preparation is reported here.

The most direct route to I was the cyclodehydration of 6-(*o*-toluoyl)chrysene (II). This ketone could be readily obtained by Friedel-Crafts acylation of chrysene with *o*-toluoyl chloride, along with an isomeric ketone which, on grounds of analogy with the acetylation of chrysene,[2] could possibly be 2-(*o*-toluoyl)chrysene.



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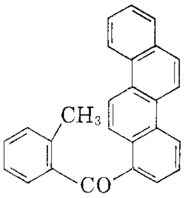
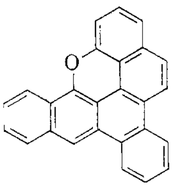
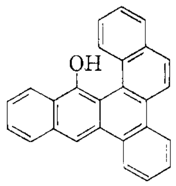


II

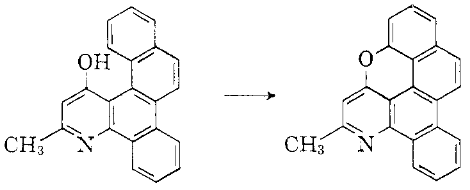
However, the pyrolysis of ketone II yielded only very small amounts of the expected hydrocarbon I, the main product of the reaction consisting of 15-oxatribenzo[a,e,jk]pyrene (III). This compound had previously been identified by Clar and Kelly[3] as one of the several products of an Elbs reaction performed on a crude noncrystalline mixture of ketones obtained from the Friedel-Crafts reaction of *o*-toluoyl chloride with chrysene. Those investigators attributed the formation of this oxygen heterocycle to the air-oxidation undergone by the hydrocarbon I during the pyrolysis. In view of the recent observation of one of the present authors[4] on the ease with which compound V is converted into compound VI by zinc dust distillation, and of the stability of the hydrocarbon I toward heat and air, we prefer to consider that compound III is formed from the intermediary anthrol IV, this anthrol arising from ketone II through rearrangement. Both the formation of anthrols and the occurrence of similar rearrangements have been reported in the literature.[5]



III



IV



V VI

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[1] A. Lacassagne, N. P. Buu-Hoï, and F. Zajdela, *Compt. rend.*, **245**, 876, 991 (1957); **246**, 1156 (1958).

[2] W. Carruthers, *J. Chem. Soc.*, 3486 (1953).

[3] E. Clar and W. Kelly, *J. Chem. Soc.*, 4163 (1957).

[4] G. C. Barrett and N. P. Buu-Hoï, *J. Chem. Soc.*, 2946 (1958).

[5] J. W. Cook, *J. Chem. Soc.*, 487 (1931); 1472 (1932); L. F. Fieser and E. Hershberg, *J. Am. Chem. Soc.*, **62**, 1640 (1940).