

*Anal.* Calcd. for  $C_{25}H_{26}$ : 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  $C_{25}H_{24}O$ : 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.

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

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

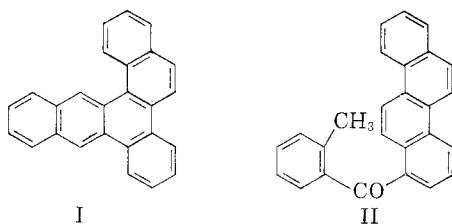
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The Elbs reaction of 6-(*o*-toluoyl)chrysene has been investigated, and found to give rise predominantly to 15-oxatribenzo[a,e,j,k]pyrene, with small amounts of benzo[a]naphtho[1,2-a]anthracene; similar compounds were obtained from the pyrolysis of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

In view of the pronounced carcinogenic activity of many hexacyclic aromatic hydrocarbons,<sup>1</sup> 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.

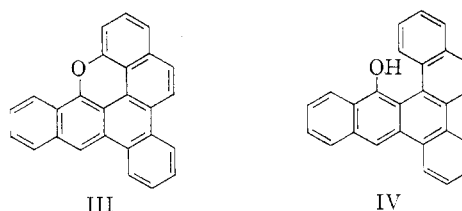
The most direct route to I was the cyclodehydration of 6-(*o*-toluoyl)chrysene (II). This ketone could



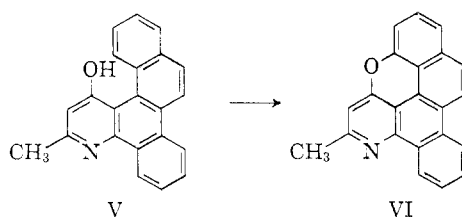
be readily obtained by Friedel-Crafts acylation of chrysene with *o*-toluoyl chloride, along with an isomeric ketone which, on grounds of analogy with the acetylation of chrysene,<sup>2</sup> could possibly be 2-(*o*-toluoyl)chrysene.

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,j,k]pyrene (III). This compound had previously been identified by Clar and Kelly<sup>3</sup> 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<sup>4</sup> 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.<sup>5</sup>

(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).

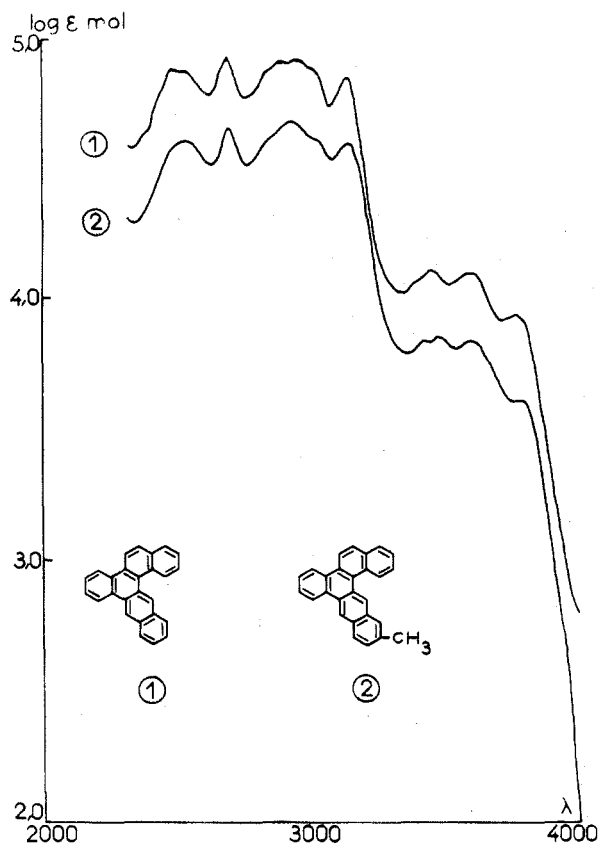
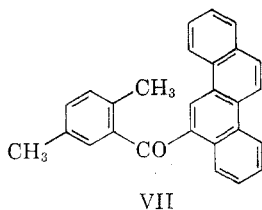


Fig. 1. Ultraviolet absorption spectra of methylated and non-methylated benzo[a]naphtho[1,2-a]anthracene

Support is given to this interpretation by the study of the Elbs reaction of 6-(2,4-dimethylbenzoyl)chrysene (VII). This ketone, readily obtained



by a Friedel-Crafts acylation of chrysene with 2,4-dimethylbenzoyl chloride, likewise gave on pyrolysis mostly a methyl-15-oxatribenzo[a,e,jk]pyrene, and only small amounts of the expected 12-methylbenzo[a]naphtho[1,2-a]anthracene. If no rearrangement were to occur during the Elbs reaction, the methyl group in both compounds should be located in position 13, or, if rearrangement does occur, in position 12. The ultraviolet absorption spectra of these two methyl compounds closely resemble that of their nonmethylated counterparts, as is shown in Figs. 1 and 2.

In the Friedel-Crafts acylation of chrysene with *o*-toluoyl chloride, three isomeric diketones could be obtained when the proportion of the acid chloride was increased to two moles per mole of chrysene. A similar reaction using 2,4-dimethylbenzoyl chloride yielded two isomeric diacylation products,

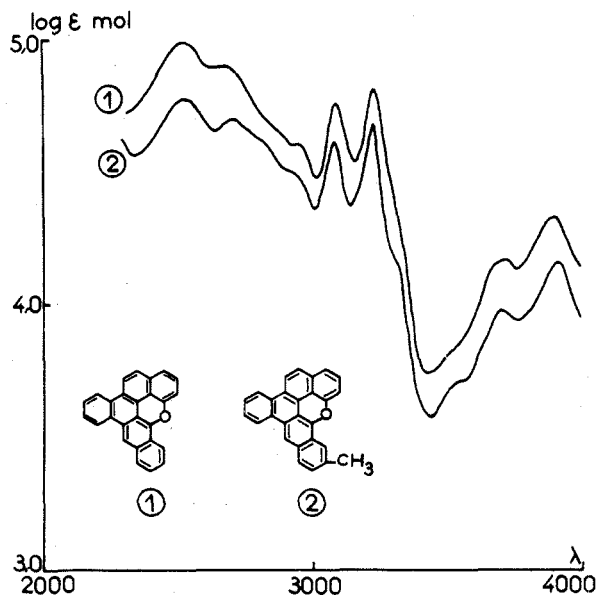


Fig. 2. Ultraviolet absorption spectra of methylated and non-methylated 15-oxatribenzo[a,e,jk]pyrene

one melting at 233°, the other at 282°; the Elbs reaction performed on the isomer, m.p. 233°, afforded a hydrocarbon, m.p. 372°, whose constitution could not be established.

#### EXPERIMENTAL

*o*-Toluoylation of chrysene. To a solution of 22.8 g. of pure chrysene and 35 g. of *o*-toluoyl chloride in 1000 ml. of dry carbon disulfide, 30 g. of finely powdered aluminum chloride was added during 10 min., with stirring. The brown-red mixture obtained was gradually brought to the boil and refluxed for 3 hr. After decomposition with ice and hydrochloric acid, 400 ml. of carbon disulfide was added, and the organic layer was washed with 3% aqueous sodium hydroxide, then with water, and dried over calcium chloride. The residue from evaporation of the solvent was taken up in 500 ml. of hot ethanol, and the insoluble fraction (26 g.) was added to the crystals obtained on cooling of the ethanolic phase and recrystallized several times from ethanol-benzene. The yield was 20 g. (58.8%) of 6-(*o*-toluoyl)chrysene (II) as fine colorless needles, m.p. 194°, giving an orange-red coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{26}H_{18}O$ : C, 90.1; H, 5.2; O, 4.6. Found: C, 90.1; H, 5.5; O, 4.6. From the mother-liquors, a very small quantity (0.1 g.) of an isomeric ketone, possibly 2-(*o*-toluoyl)chrysene, could be isolated, and was recrystallized from ethanol-benzene in colorless leaflets, m.p. 230°, giving a brown-yellow coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{26}H_{18}O$ : C, 90.1; H, 5.2. Found: C, 89.8; H, 5.2.

*Elbs reaction of ketone II.* Eleven grams of the foregoing ketone was refluxed for 30 min., and the reaction product vacuum-fractionated, giving a pale yellow, low-boiling resin A (6.5 g.), and a brown-red, higher-boiling resin B (1.5 g.). Fractional crystallization of A from benzene furnished the less soluble compound III (1 g.), orange-yellow needles, m.p. 290–293°. Vacuum sublimation afforded the pure compound in the form of shiny yellow needles, m.p. 296°, giving a raspberry red coloration in sulfuric acid. Clar and Kelly<sup>8</sup> reported m.p. 288–289° for this compound.

*Anal.* Calcd. for  $C_{26}H_{14}O$ : C, 91.2; H, 4.1; O, 4.7. Found: C, 91.4; H, 4.3; O, 4.6. Crystallization of fraction B from toluene gave a further crop (0.4 g.) of this compound.

Concentration of the benzene mother-liquors gave (1) chrysene (1 g.), and (2) a resin which was recrystallized from methyl ethyl ketone to form *benzo[a]naphtho[1,2-a]anthracene* (I), colorless needles (50 mg.), m.p. 193°, giving no coloration in sulfuric acid. Beyer and Richter,<sup>6</sup> who prepared this hydrocarbon by a different method, reported m.p. 185–186°.

*Di-o-toluoylation of chrysene.* A solution of 22.8 g. of chrysene and 35 g. of *o*-toluoyl chloride in 1000 ml. of carbon disulfide was treated with 40 g. of aluminum chloride and the mixture left for 2 days at room temperature, then refluxed for 150 min. After decomposition with ice and hydrochloric acid, 1000 ml. of methylene chloride was added, and the organic layer treated in the usual way. The residue from evaporation of the solvent was a brown amorphous mass, which was treated with 100 ml. of hot acetone. The crystals that formed after cooling in the refrigerator were submitted to fractional recrystallization from methyl ethyl ketone, to yield first a portion (5 g.) melting at about 250°, which, after a second recrystallization, formed pale yellow prisms of a *di-o-toluoylchrysene*, m.p. 256°, giving a brown-red coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{33}H_{24}O_2$ : C, 87.6; H, 5.4; O, 7.1. Found: C, 87.8; H, 5.3; O, 7.0.

A second, more soluble *di-o-toluoylchrysene* (1 g.), was recrystallized from methyl ethyl ketone, then from acetic acid, in fine, cream-colored needles, m.p. 231°, giving an orange-yellow coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{33}H_{24}O_2$ : C, 87.6; H, 5.4; O, 7.1. Found: C, 87.7; H, 5.4; O, 6.9.

A third isomeric *di-o-toluoylchrysene* (5 g.), the most soluble of the three, was recrystallized from benzene to give colorless prisms, m.p. 213°, whose coloration in sulfuric acid was likewise orange-yellow.

*Anal.* Calcd. for  $C_{33}H_{24}O_2$ : C, 87.6; H, 5.4; O, 7.1. Found: C, 87.9; H, 5.3; O, 6.9.

*Monoacylation of chrysene with 2,4-dimethylbenzoyl chloride.* A mixture of 22.8 g. of chrysene, 33.7 g. of 2,4-dimethylbenzoyl chloride, and 760 ml. of carbon disulfide was treated with 26.7 g. of aluminum chloride; after a 22-hr. stand at room temperature, the mixture was refluxed for 1 hr., then treated in the usual way. A resinous product was obtained which on crystallization first from methyl ethyl ketone, and then from acetic acid yielded 6-(2,4-dimethylbenzoyl)chrysene (VII), colorless needles (16.5 g.), m.p. 146°, whose coloration in sulfuric acid was crimson.

*Anal.* Calcd. for  $C_{27}H_{20}O$ : C, 89.9; H, 5.6. Found: C, 89.5; H, 5.6.

*Pyrolysis of compound VII.* This operation was performed on 9 g. of the ketone, as for ketone II, to furnish a lower-

boiling portion (0.7 g.) which was identical with chrysene, and a higher-boiling, vitreous product (5.2 g.) which was recrystallized several times from toluene, giving 0.7 g. of 12- or 13-methyl-15-oxatribenzo [a,e,jk]pyrene, stumpy yellow needles, m.p. 244°, whose coloration in sulfuric acid was chocolate brown.

*Anal.* Calcd. for  $C_{27}H_{16}O$ : C, 91.0; H, 4.5. Found: C, 91.0; H, 4.7.

From the mother-liquors, 0.13 g. of a 12- or 13-methylbenzo[a]naphtho[1,2-a]anthracene was isolated; this hydrocarbon was recrystallized from hexane to afford fine colorless needles, m.p. 226°, giving no coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{27}H_{18}$ : C, 94.7; H, 5.3. Found: C, 94.8; H, 5.1.

*Diacylation of chrysene with 2,4-dimethylbenzoyl chloride.* A mixture of 19 g. of chrysene, 23 g. of 2,4-dimethylbenzoyl chloride, and 650 ml. of carbon disulfide was treated with 22 g. of aluminum chloride; after a 2-day stand at room temperature, followed by 2 hr. refluxing, the reaction mixture was worked up in the usual way. The product was a viscous resin which crystallized on trituration with methyl ethyl ketone. The solid thus obtained (10.3 g.) was treated with 550 ml. of acetic acid, leaving an insoluble residue which was recrystallized from benzene, to give a first *di-(2,4-dimethylbenzoyl)chrysene* (1.9 g.), yellowish prisms, m.p. 282°, with a crimson coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{36}H_{28}O_2$ : C, 87.8; H, 5.7. Found: C, 87.3; H, 5.8.

From the benzene mother-liquors, the more soluble isomeric *di-(2,4-dimethylbenzoyl)chrysene* was isolated, and recrystallized first from ethanol, then from acetic acid. The yield was 6 g. of fine yellowish prisms, m.p. 233°, with an orange-red coloration in sulfuric acid.

*Anal.* Calcd. for  $C_{36}H_{28}O_2$ : C, 87.8; H, 5.7. Found: C, 87.5; H, 5.8.

The Elbs reaction performed on this last diketone (4.5 g.) yielded an *octacyclic hydrocarbon* which crystallized from toluene in almost colorless leaflets (0.4 g.), m.p. 372°. That this hydrocarbon is almost colorless and gives no halochromism in sulfuric acid suggests that it does not contain a naphthacene arrangement in its molecule.

*Anal.* Calcd. for  $C_{27}H_{18}$ : C, 94.7; H, 5.3. Found: C, 94.6; H, 5.3.

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(6) H. Beyer and J. Richter, *Ber.*, **73**, 1319 (1940).