

## 126. Structures of Degradation Products of Picene.

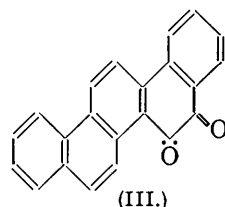
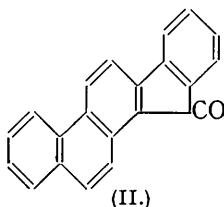
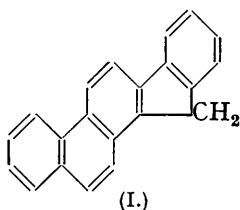
By J. W. Cook.

The main constituent of "picylene ketone" has been isolated and shown to be 2':1'-naphtha-1:2-fluorenone (II). This implies that picenequinone consists essentially of the unsymmetrical quinone (III).

THE analytical evidence for the structure of picene consists in its degradation through icenequinone to "picylene ketone" and picenic acid, from which 2:2'-dinaphthyl was obtained by decarboxylation (Bamberger and Chattaway, *Annalen*, 1895, **284**, 52). The synthesis of picene by several methods shows quite conclusively that it is 1:2:7:8-dibenzphenanthrene, and hence picylene ketone should be 1:2:7:8-dibenzfluorenone or (less probably) 1:2:6:7-dibenzfluorenone. The preceding paper describes three dibenzfluorenones shown to be derived from 2:2'-dinaphthyl and none of these corresponds in properties with picylene ketone. As only three such ketones are theoretically possible, reinvestigation of picylene ketone became necessary.

This has now been done and has been much facilitated by the great kindness of Dr. F. D. Chattaway, F.R.S., who placed at the author's disposal a specimen of picylene ketone which he prepared nearly half a century ago. By means of the modern chromatographic technique this material, which melted at about the temperature (185.5°) quoted by Bamberger and Chattaway, was separated into a number of fractions, the chief of which consisted of a well-crystallised golden-yellow ketone, m. p. 206°. Although this is close to the m. p. of 1:2:6:7-dibenzfluorenone (preceding paper), the mixed m. p. showed a marked depression, and the two ketones differed in their colour reactions with concentrated sulphuric acid. By reduction of picylene ketone with hydriodic acid and phosphorus, Bamberger and Chattaway obtained a hydrocarbon, m. p. 306°. As this method of reduction is sometimes attended by molecular rearrangement, the purified specimen of picylene ketone was reduced with hydrazine hydrate at 220—240° (it was subsequently noted that Bamberger and Chattaway had also obtained their hydrocarbon by reduction with phenylhydrazine). The product was a hydrocarbon, m. p. 335° (corr.), which showed no depression when mixed with synthetic picene. This behaviour recalled that of 2':1'-naphtha-1:2-fluorene (I) (Cook, Hewett, Mayneord, and Roe, J., 1934,

1727), with which, in fact, the new hydrocarbon proved to be identical. Moreover, the purified picylene ketone, m. p. 206°, was found identical with 2' : 1'-naphtha-1 : 2-fluorenone (II). This finding necessitates revision of the symmetrical structure commonly attributed to picenequinone, which must now be regarded as consisting essentially of (III).



The purified specimen of picylene ketone gave, on fusion with potash, a mixture of acids, from which was isolated a compound agreeing in its m. p. with the picenic acid of Bamberger and Chattaway. This acid, which differed from the two 2 : 2'-dinaphthyl-carboxylic acids of Martin, is clearly derived from 2-phenylphenanthrene, and the isolation of 2 : 2'-dinaphthyl from the products of its decarboxylation must be attributed to the presence of impurity in the picenic acid used by Bamberger and Chattaway.

#### EXPERIMENTAL.

All m. p.'s are corrected.

*Purification of Picylene Ketone.*—The material supplied was an orange microcrystalline powder, m. p. 176—184°. Purification by sublimation was first attempted and the substance (0.75 g.) was sublimed at 175—200°/0.05 mm. The more volatile portion of the sublimate (0.25 g.) was uniformly orange in colour and highly crystalline. Repeated crystallisation from ethyl acetate and from benzene gave orange leaflets, m. p. 197.5—201°. Purification was obviously not complete and the material from the liquors was combined with the less volatile sublimate (m. p. 179—184°) and dissolved in a mixture of benzene and ligroin. The solution was passed through a column of alumina (100 g.), and the chromatogram developed with ligroin. There were two well-marked visible zones, the principal one consisting of material less readily adsorbed than the other. Elution was effected by passing through the column mixtures of benzene and ligroin progressively enriched in benzene, and finally pure benzene. The following fractions were obtained by concentrating the eluates and adding light petroleum :

i. A hydrocarbon fraction (40 mg.) which crystallised from benzene in colourless leaflets, m. p. 278—282° (Found : C, 94.6 ; H, 5.8%). There was insufficient material for purification.

ii. Colourless leaflets (20 mg.) which, after recrystallisation from benzene, had m. p. 295—300°, not depressed by picene.

iii. Golden-orange leaflets (20 mg.), m. p. 203—204°. This was essentially the same as fraction iv.

iv. Golden-orange leaflets (0.25 g.), m. p. 204—205°.

v. Golden-orange leaflets (65 mg.), m. p. 187—188°.

vi. An orange powder (35 mg.) which after crystallisation from ethyl acetate had m. p. 225—240°.

vii. A canary-yellow powder (5 mg.) which after recrystallisation from benzene had m. p. 265—275°.

Fraction iv, which came from the main coloured zone of the column, was recrystallised from ethyl acetate and formed golden-yellow leaflets, m. p. 205.5—206.5° (Found : C, 90.0 ; H, 4.45.  $C_{21}H_{12}O$  requires C, 90.0 ; H, 4.3%). The mixed m. p. with synthetic 2' : 1'-naphtha-1 : 2-fluorenone (m. p. 210°) was 207—208°. Both specimens gave an intense permanganate purple solution in concentrated sulphuric acid, the colour soon changing to carmine-red.

*Reduction of Purified Picylene Ketone.*—A suspension of the ketone (100 mg.) in 50% hydrazine hydrate (2 c.c.) was heated in a sealed tube at 220—240° for 9 hours. The product, obtained in good yield, was recrystallised twice from benzene and then formed colourless leaflets, m. p. 335° (Found : C, 94.7 ; H, 5.5.  $C_{21}H_{14}$  requires C, 94.7 ; H, 5.3%). The m. p. was not depressed by synthetic 2' : 1'-naphtha-1 : 2-fluorene, m. p. 338—339°, and the identification was completed by preparation of the 2 : 7-dinitroanthraquinone complex, m. p. 253—255° alone or mixed with a synthetic specimen.

*Fusion of Picylene Ketone with Potash.*—The purified ketone (100 mg.) was added to potassium

hydroxide (2 g.) at 240°, and the melt stirred at 240—250° for  $\frac{1}{2}$  hour. The resulting somewhat resinous mixture of acids was dissolved in aqueous acetic acid. The solution slowly deposited 25 mg. of crystal nodules, which, after recrystallisation from benzene, formed colourless, microscopic, elongated plates, m. p. 207—209°, and gave with sulphuric acid the colour changes characteristic of 2' : 1'-naphtha-1 : 2-fluorenone. Bamberger and Chattaway give m. p. 201° (uncorr.) for picenic acid. The acid recovered from the acetic acid mother-liquors was recycled by 3 hours' heating at 100° with 80% sulphuric acid. The resulting ketone, crystallised from acetic acid, had m. p. 205—206°, not depressed by picylene ketone. There was no evidence of the formation in this series of changes of the isomeric 1' : 2'-naphtha-2 : 3-fluorenone (Cook *et al.*, J., 1935, 1324) which might arise as an alternative.

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