

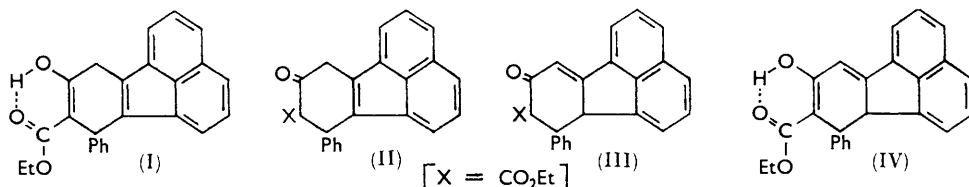
284. *The Interaction of 2-Benzylideneacenaphthen-1-one and Ethyl Acetoacetate.*

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2-Benzylideneacenaphthen-1-one and ethyl acetoacetate in the presence of alkali yield the chelated ester (I), the isomerisation of which has been studied. Heating of the ester (I) with sulphuric acid results in hydrolysis and decarboxylation with the formation of 6b,7,8,9-tetrahydro-9-oxo-7-phenylfluoranthene (VI) which, on reduction with potassium borohydride and dehydrogenation of the product, yields 9-hydroxy-7-phenylfluoranthene (VIIa) in the form of the orthoboric ester.

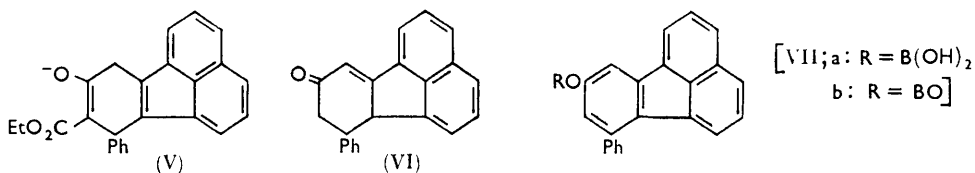
BENZYLIDENEACENAPHTHENEONE condensed with ethyl acetoacetate in the presence of alkali to give a mixture, of which only one component was obtained pure, as yellow needles, m. p. 178—180°. This gave a purple colour with ferric chloride and exhibited infrared bands at 1663 (chelated ester) and 1618 and 1575 cm^{-1} (ethylenic linkages), but no other carbonyl band. Structure (I) for this compound is confirmed by its ultraviolet spectrum, which resembles that of acenaphthylene. It slowly forms a 2,4-dinitrophenylhydrazone, probably following tautomerisation to a ketone (II) or (III). Compound (I), with sulphuric acid, yielded an unstable substance, containing an $\alpha\beta$ -unsaturated ketonic group

(1658 cm^{-1}) and an unconjugated ester grouping (1737 cm^{-1}), which reverted on crystallisation to the original substance. It probably has structure (III). Chromatography of the mother liquors from this crystallisation yielded an isomer, m. p. 160—160.5°, which was also occasionally obtained in small yield along with compound (I) in the original condensation. The formula (IV) is assigned to this compound, since it shows only one



carbonyl band (1655 cm^{-1}), attributed to a chelated ester grouping, and a double-bond absorption (1583 cm^{-1}), but its ultraviolet spectrum differs from that of compound (I). Both esters, (I) and (IV), showed the same spectrum in ethanolic potassium hydroxide.

These results are similar to, but not so clear-cut as those obtained with the corresponding hydrophenanthrene and hydrofluorene compounds formed in reactions between ethyl acetoacetate and 2-benzylidene-1-tetralone or 2-benzylideneindan-1-one.¹ We therefore conclude, by analogy, that compounds (III) and (IV) are probably not merely tautomers but differ in stereochemistry at C-7, and that the spectrum shown by compounds (I) and (IV) in alkaline solution is that of the enolate ion (V) corresponding to ester (I).



The chelated ester (I), with boiling sulphuric acid, underwent hydrolysis and decarboxylation to give 6b,7,8,9-tetrahydro-9-oxo-7-phenylfluoranthene (VI) whose ultraviolet spectrum is different from that of acenaphthylene and which contains an $\alpha\beta$ -unsaturated ketonic group (1665 cm^{-1}). This ketone was reduced by potassium borohydride and the product dehydrogenated by palladium-charcoal to give yellow crystals, m. p. 199—202° (m. p. 321—323° after resolidification). The two substances contain boron, and are probably the orthoboric ester (VIIa) and the metaboric ester (VIIb) formed from it by loss of water. This is supported by the analysis of the higher-melting substance, by the similarity of the two ultraviolet spectra to one another and to that of fluoranthene, and by the fact that the esters with sodium hydroxide yield sodium borate. It appears that the formation of a boric ester "protects" the oxygen during the aromatisation.

In the course of the work the reduction of benzylideneacenaphthenone to 2-benzylacenaphthen-1-one and 1-benzylacenaphthene was effected.

EXPERIMENTAL

Reduction of 2-Benzylideneacenaphthen-1-one.—The ketone (1 g.), in ethylene glycol (20 ml.), hydrazine hydrate (0.5 g.), and potassium hydroxide (1.0 g.), was heated at 100° (0.5 hr.) and then boiled (0.5 hr.). Acidification, ether extraction, and evaporation gave 1-benzylacenaphthene (0.15 g.), plates, m. p. 149—150° (from light petroleum) (Found: C, 94.1; H, 6.0. C₁₉H₁₄ requires C, 94.2; H, 5.8%).

The ketone (1 g.) in ethyl acetate (200 ml.) was shaken with Adams platinum catalyst (5 mg.) and hydrogen at 1 atm. pressure. Evaporation of the solvent gave 2-benzylacenaphthen-1-one (0.65 g.), plates, m. p. 81—82° (from ethanol) (Found: C, 88.0; H, 5.4. C₁₉H₁₄O requires

¹ Anderson and Leaver, *J.*, 1962, 450.

C, 88.3; H, 5.5%); λ_{\max} 218, 245, 320, 341 μ ($\log \epsilon$ 4.55, 4.3, 3.74, 3.74), λ_{\min} 233, 273, 330 μ ($\log \epsilon$ 3.16, 2.92, 3.72) (both in ethanol), similar to that of acenaphthen-1-one.

Reaction of 2-Benzylideneacenaphthen-1-one and Ethyl Acetoacetate.—Sodium ethoxide solution (10–15 ml.), prepared from sodium (2 g.) and ethanol (40 ml.), was added to acenaphthen-1-one (15 g.) and freshly distilled benzaldehyde (19 g.) in ethanol (1 l.). After 2 days the benzylidene compound (44%) separated in golden plates, m. p. 113.5–115.5° (lit.,² 117°), λ_{\max} 235, 306, 325 μ ($\log \epsilon$ 4.58, 4.44, 4.42). The almost quantitative yield claimed by previous workers² could not be obtained. The benzylidene derivative (5.5 g.) was added to ethyl acetoacetate (3.35 g.) in ethanol (55 ml.) containing sodium (0.66 g.). After 20 hr. the filtered solution was acidified with dilute hydrochloric acid and gave *ethyl 7,10-dihydro-9-hydroxy-7-phenylfluoranthene-8-carboxylate* (33%), yellow crystals, m. p. 178–180° (from benzene–ethanol) (Found: C, 81.0; H, 5.7. $C_{25}H_{20}O_3$ requires C, 81.5; H, 5.5%); λ_{\max} 232, 260, 303 (infl.), 310, 323, 333, 340 μ ($\log \epsilon$ 4.72, 4.00, 3.8, 4.00, 4.7, 3.82, 3.80) in ethanol; 227, 315 μ ($\log \epsilon$ 4.76, 4.52) in ethanol containing 0.024% of sodium. Attempts to prepare a dinitrophenylhydrazone by Brady's method³ were unsuccessful, but when the substance was heated overnight with 2,4-dinitrophenylhydrazine and a little hydrochloric acid⁴ a 2,4-dinitrophenylhydrazone separated as red prisms, m. p. 246–248° (from tetralin) (Found: N, 10.1. $C_{31}H_{24}N_4O_6$ requires N, 10.2%).

The ester (2.0 g.) in ethanol (2 ml.) was added to concentrated sulphuric acid (20 ml.) and the mixture cooled and after 5 min. poured into water (200 ml.). After 1/2 hr. the precipitate (probably II) was washed and dried. Crystallisation from ethyl acetate gave starting material. Evaporation of the ethyl acetate from the filtrates gave a residue which was chromatographed on alumina deactivated with 10% of water containing 10% of acetic acid, in light petroleum–benzene, to give *ethyl 6b,7-dihydro-9-hydroxy-7-phenylfluoranthene-8-carboxylate*, yellow crystals, m. p. 160–160.5° (Found: C, 81.9; H, 5.3. $C_{25}H_{20}O_3$ requires C, 81.5; H, 5.5%); λ_{\max} (in ethanol) 233, 260, 267, 300, 308, 323, 347, 365 μ ($\log \epsilon$ 4.57, 4.07, 4.06, 4.42, 4.42, 4.10, 4.08, 3.68, 3.74).

The ethyl ester (I) (1.5 g.) was boiled for 15 min. in acetic acid (5 ml.), concentrated sulphuric acid (2.5 ml.), and water (1.2 ml.), and poured into water. Extraction with ether, followed by washing with sodium carbonate and evaporation of solvent, gave 6b,7,8,9-tetrahydro-9-oxo-7-phenylfluoranthene, yellow crystals, m. p. 185–186.5° (from benzene–light petroleum) (Found: C, 88.6; H, 5.6. $C_{22}H_{16}O$ requires C, 89.2; H, 5.4%); λ_{\max} (in ethanol) 227, 258, 295, 362 μ ($\log \epsilon$ 4.48, 4.32, 3.70, 4.14), similar to the spectrum of 1-naphthylideneacetone.⁵

The ketone (1.6 g.) was heated (1½ hr.) in dioxan (50 ml.) with potassium borohydride (0.5 g.). Acidification and addition of water gave an oil which, with sodium hydroxide, yielded sodium borate, but no other crystalline derivative. The oil (0.5 g.) was heated at 280° for 0.5 hr. with 20% palladium–charcoal. The residue, in benzene–light petroleum, was chromatographed on alumina. Elution with light petroleum gave the orthoborate of 7-phenylfluoranthene-9-ol (20 mg.), yellow needles, m. p. 199–202° (from benzene–light petroleum), giving on further heating a viscous liquid which solidified, m. p. 321–323°. Slow heating of the lower-melting substance resulted in only very slight melting at 220°. Drying the compound overnight gave the *metaborate* of 7-phenylfluoranthene-9-ol, yellow needles, m. p. 321° (from benzene), blue fluorescence (Found: C, 83.1; H, 4.5. $C_{22}H_{13}BO_2$ requires C, 82.5; H, 4.1%). The compound gave a blue colour with *p*-nitrobenzeneazochromotropic acid reagent. Both borates exhibited λ_{\max} (in chloroform) 245, 302, 328, 390 μ , with an absorption curve resembling that of fluoranthene.

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² Graebe and Jequier, *Annalen*, 1896, **290**, 204.

³ Brady, *J.*, 1931, 756.

⁴ Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955.

⁵ Wilds, Beck, Close, Djerassi, Johnson, and Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1985.