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SYNTHESIS OF 1-ETHYL AND 5-ETHYL AZULENES

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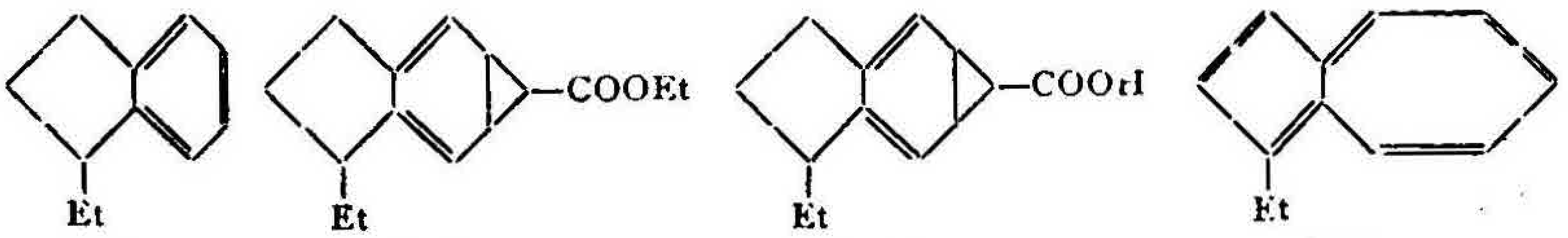
All the five possible monomethyl azulenes have been synthesised.[1] However, in the case of monoethyl azulenes only two are known, *viz.*, 2-ethyl[2]- and 4-ethyl[3]-azulenes. Hence the synthesis of 1-ethyl- and 5-ethylazulenes was undertaken. Both of them have been synthesised starting from the corresponding indane and enlarging the six-membered ring, using diazoacetic ester.

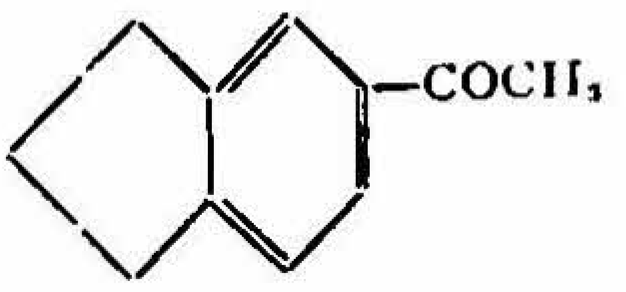
The synthesis of 1-ethylazulene (IV) was carried out according to the scheme given below.



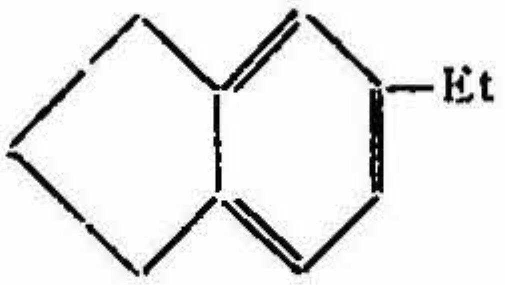
(I) (II) (III) (IV)

1-Ethylindane (I) was condensed with diazoacetic ester.[4] The resulting condensation product (II) was hydrolysed to the corresponding acid (III) which was subjected to simultaneous decarboxylation and dehydrogenation by heating with 10% palladium-charcoal over a free flame when a blue oil was obtained. 1-Ethyl azulene (IV) was isolated from the blue distillate using the phosphoric acid extraction method followed by chromatography over alumina. 1-Ethylazulene (IV) is characterised as its *s*-trinitrobenzene complex, m.p. 112–13·5°, picrate, m.p. 92–94°, and by the absorption maxima at 610 mμ (log ϵ, 2·45), 668 mμ (log ϵ, 2·35) and 740 mμ (log ϵ, 1·89).

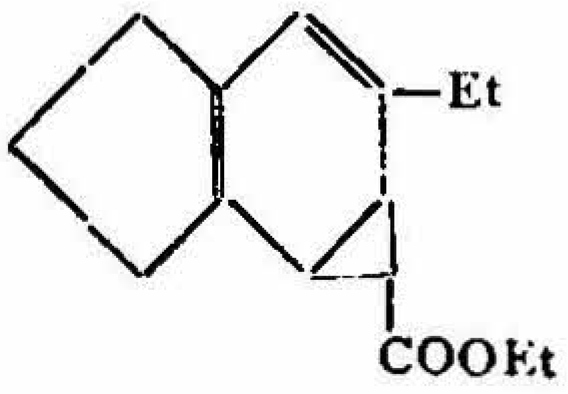
The synthesis of 5-ethylazulene was carried out according to the scheme outlined below.



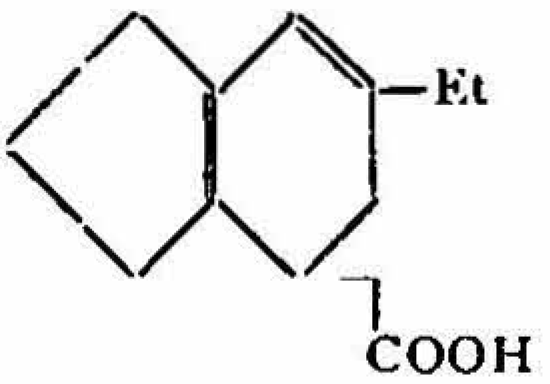
(V)



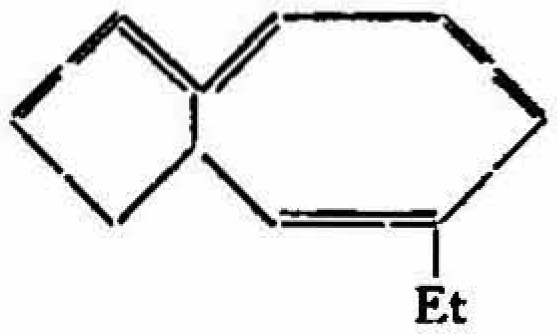
(VI)



(VII)



(VIII)



(IX)

Clemmensen reduction of 5-acetylindane (V) using alcohol as miscible solvent gave 5-ethylindane (VI). The latter was treated with diazoacetic ester according to the method of Pfau and Plattner.[4] The condensation product should have the structure[5] (VII). The ester (VII) was hydrolysed to the corresponding acid (VIII). The free acid was subjected to simultaneous decarboxylation and dehydrogenation

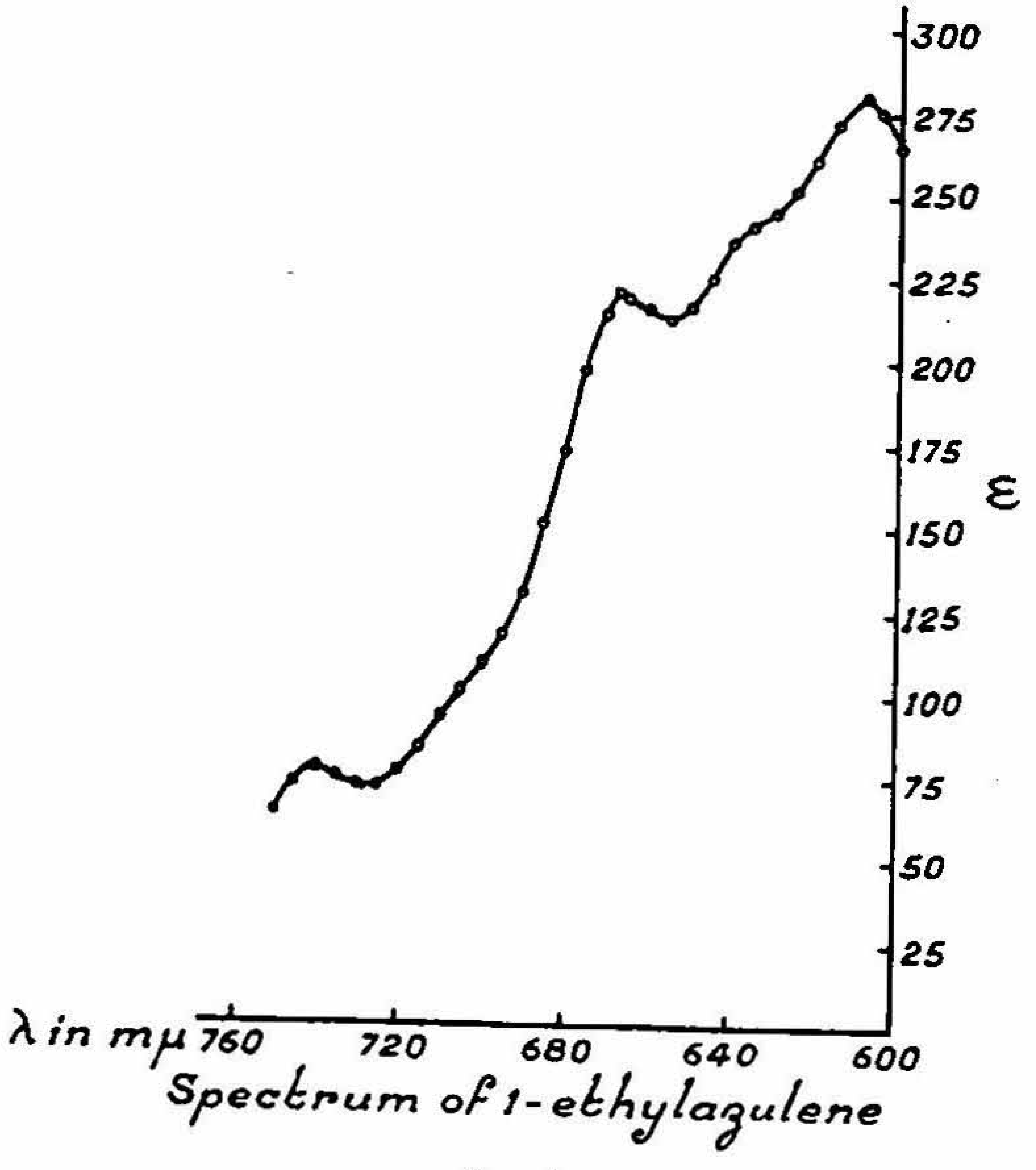


FIG. 1

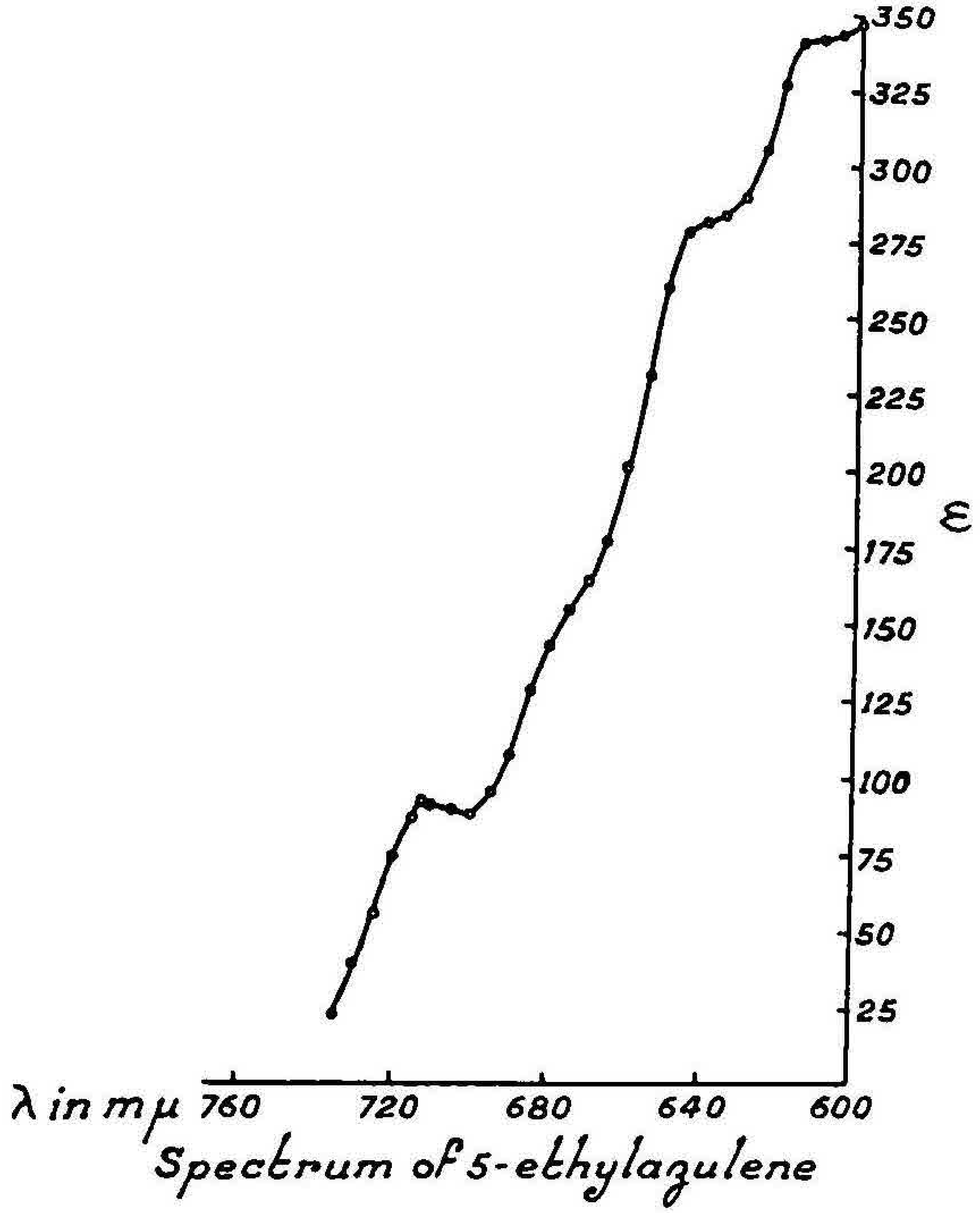


FIG. 2

by heating with 10% palladium-charcoal over a free flame when a deep blue oil was obtained. From this oil 5-ethylazulene was isolated. It was characterised as its *s*-trinitrobenzene complex, m.p. 97–97·5° and by the absorption maximum at 713 mμ (log ε, 1·96).

EXPERIMENTAL[*]

Condensation of 1-*ethylindane* (*I*) *with diazoacetic ester*

To 40 g. of 1-ethylindane kept heated at 130° was added dropwise 8 g. of diazoacetic ester during the course of fifteen minutes. The temperature was maintained at 130° for half an hour and then gradually raised to 170° at which temperature it was maintained for three and a half hours. The reaction mixture was allowed to cool and fractionated at 12 mm. The distillation was stopped when all the 1-ethylindane had distilled over. The experiment was repeated with the recovered 1-ethylindane twice. The residues obtained during the above fractionations were then combined and distilled when 16·6 g. of the ester (II), b.p. 150–55°/4 mm.

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[*] Melting points and boiling points are uncorrected.

was obtained (Found: C, 79·1%, H, 8·8%; $C_{15}H_{20}O_2$ requires C, 77·6%; H, 8·6%). The high value for carbon may be due to the contamination of the ester with unreacted 1-ethylindane.

Hydrolysis of the ester (II)

16 g. of the ester (II) on saponification with alcoholic potassium hydroxide gave 8·2 g. of the acid (III), b.p. 170–175°/3 mm. (Found: 76·17%; H, 7·75%; $C_{13}H_{16}O_2$ requires C, 76·5%; H, 7·8%).

Decarboxylation and dehydrogenation of the acid (III)

7·8 g. of the acid (III) mixed with 0·9 g. of 10% palladium-charcoal was heated in a pyrex distilling flask over a free flame when 6 g. of a blue distillate was obtained. The distillate was taken up in petroleum ether (b.p. 40–60°) and dried over anhydrous calcium chloride. The dried petroleum ether solution was shaken repeatedly with small amounts of 85% phosphoric acid till the petroleum ether layer was almost colourless. The phosphoric acid extract was cooled in ice, diluted with ice-cold water and extracted with ether. The ether extract was dried over calcium chloride. The residue left after removing the ether was taken up in low-boiling petroleum ether (30°–60°) and passed down a column of alumina. The elution was carried out with a mixture (1: 1) of benzene and petroleum ether. The azulenic portion was collected separately. Removal of the solvent gave 220 mg. of strong smelling deep blue oil.

To 150 mg. of the deep blue oil in 8 c.c. of alcohol was added a hot alcoholic solution of 170 mg. of *s*-trinitrobenzene. The mixture was warmed on the water-bath for a short time and left aside at room temperature for 24 hours. 160 mg. of needle-shaped crystals (m.p. 110–12°) separated out. After two recrystallisations from alcohol the melting point rose to 112–13·5°. Further recrystallisation did not raise the melting point (Found: N, 11·7%; $C_{18}H_{15}O_6$ requires N, 11·4%).

Regeneration of 1-ethylazulene (IV)

From 70 mg. of recrystallised *s*-trinitrobenzene adduct of 1-ethylazulene 26 mg. of 1-ethylazulene was obtained as a deep blue oil, following the technique of Pfau and Plattner[6] (Found: C, 92·2%; H, 8·1%; $C_{12}H_{12}$ requires C, 92·3%; H, 7·7%). The spectrum of an alcoholic solution of the azulene was taken using a Beckman spectrophotometer (see Fig. 1).

Acetylation of indane

Indane was acetylated under the conditions described by Braun[7] and co-workers. The acetyl indane thus obtained had $b_{11}=132\text{–}34°$; $n_D^{24}=1·5595$; $d_D^{24}=1·056$ (lit: b_{11} 134–35°).

Clemmensen reduction of 5-acetylindane (V)

A solution of 50 g. of 5-acetylindane in 250 c.c. of ethanol was added in portions over a period of four hours to a refluxing mixture of 100 c.c. of water, 40 c.c. ethanol, 250 c.c. of concentrated hydrochloric acid and 350 g. of amalgamated zinc. After addition was complete the mixture was refluxed for ten hours, during which time 200 c.c. of concentrated hydrochloric acid was added in portions. On working up the reaction mixture 35 g. of 5-ethylindane was isolated, b.p. 114–16°/24 mm.; $n_D^{26} = 1 \cdot 5262$; $d_4^{26} = 0 \cdot 933$ (Found: C, 90·36%; H, 9·6%; $C_{11}H_{14}$ requires C, 90·4%; H, 9·6%).

Condensation of 5-ethylindane (VI) with diazoacetic ester

40 g. of 5-ethylindane on condensation with diazoacetic ester under the aforementioned conditions gave 22·1 g. of a light red liquid, b.p. 145–150°/2 mm. The colour almost disappeared on standing (Found: C, 78·0%; H, 8·2%; $C_{15}H_{20}O_2$ requires C, 77·6%; H, 8·6%).

Hydrolysis of the ester (VII)

The ester (VII) (20 g.) on saponification with alcoholic alkali furnished 13·4 g. of a dark coloured acid, b.p. 167–70°/3 mm. (Found: C, 76·5%; H, 7·8%; $C_{13}H_{16}O_2$ requires C, 76·3%; H, 8·1%).

Decarboxylation and dehydrogenation of the acid (VIII)

11·4 g. of the acid (VIII) on decarboxylation and dehydrogenation as before furnished 300 mg. of 5-ethylazulene as a strongly smelling deep blue oil. It gave with *s*-trinitrobenzene, a complex m.p. 97–7·5 (from alcohol) (Found: C, 59·0%; H, 4·3%; N, 11·9%; $C_{18}H_{15}N_3O_6$ requires C, 58·5%; H, 4·7%; N, 11·4%). For spectroscopic work, 5-ethylazulene was regenerated from its *s*-trinitrobenzene complex following the technique or Pfau and Plattner[6] (see Fig. 2) (Found: C, 92·1%, H, 8·0%; $C_{12}H_{12}$ requires C, 92·3%, H, 7·7%).

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