Cyclisation of Arylbutyric Acids with Polyphosphoric Acid. The By-products.

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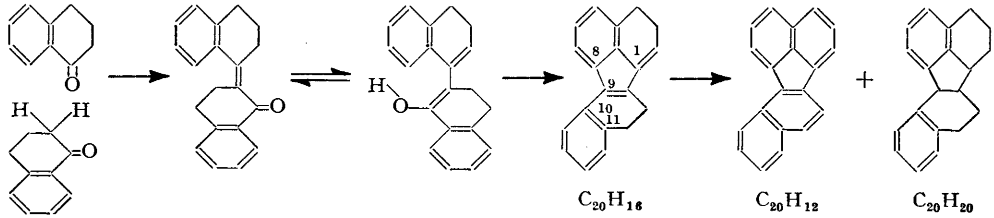
Ring closures of arylbutyric acids may rapidly and advantageously be carried out with polyphosphoric acid at temperatures of 150—170°, but prolonged heating with the reagent converts the resulting tetralones into complex products, in some cases 10 : 11-benzofluoranthenes.

The use of " polyphosphoric acid " (a solution of phosphoric oxide in syrupy phosphoric acid) introduced by Koebner and Robinson (*J.*, 1938, 1995) has become general for ring-closures of aryl-propionic, -butyric, and -valeric acids (Birch, Jaeger, and Robinson, *J.*, 1945, 585; Bachmann and Horton, *J. Amer. Chem. Soc.*, 1947, **69**, 58; Snyder and Werber, *ibid.*, 1950, **72**, 2962, 2965; Gilmore and Horton, *ibid.*, 1951, **73**, 1411; Snyder and Roeske, *ibid.*, 1952, **74**, 5820; Mosby, *ibid.*, p. 2564; Koo, *ibid.*, 1953, **75**, 1891; Evans and Smith, *J. Inst. Petrol.*, 1951, **37**, 80).

In an investigation of the ring-closure of γ-2 : 4-dimethylphenylbutyric acid to 1 : 2 : 3 : 4-tetrahydro-5 : 7-dimethyl-1-oxonaphthalene, Evans and Smith (*loc. cit.*) found that the most satisfactory conditions (considering yield, economy of reagents, and speed of working) were (*a*) use of 1 part of the butyric acid to 10 parts of polyphosphoric acid, (*b*) a temperature between 150° and 170°, and (*c*) a reaction time of 2—3 minutes. Under these conditions the cyclisation of a series of γ-mono- and -di-methylphenylbutyric acids gave 80—93% yields of tetralones. In no case was there detected any migration of the substituents in the aromatic ring (cf. Mosby, *J. Org. Chem.*, 1953, **18**, 485.)

In those ring-closures in which the yields of tetralones had fallen much below 90% it was noticed that if the temperature exceeded 170° or the reaction time 3 minutes (even at 160—170°) rapid formation of by-products resulted. Further, if α-tetralone itself was heated at 170° with polyphosphoric acid, similar oily by-products were formed. From the by-product (b. p. 200°/0·025 mm.) a colourless hydrocarbon, $C_{20}H_{20}$, of m. p. 149° and also a yellow hydrocarbon, $C_{20}H_{12}$, m. p. 163—164° (picrate, m. p. 194—195°), were obtained.



As Nenitzescu and Avram (*J. Amer. Chem. Soc.*, 1950, **72**, 3486) have shown that 10 : 11-benzofluoranthene (obtained from tetralin and phosphoric oxide followed by dehydrogenation, or synthesised by three distinct routes) melts at 165° and yields a picrate of m. p. 195°, the course of the reaction with polyphosphoric acid is probably as shown in the annexed scheme. The ketone initially produced reacts in its enol form, losing water, to give a tetrahydro-10 : 11-benzofluoranthene which then disproportionates to the benzofluoranthene and an octahydro-compound. If this mechanism is correct any methyltetralone with a free 8-position should yield a benzofluoranthene. During the formation (by ring-closure of the arylbutyric acids) of 1 : 2 : 3 : 4-tetrahydro-4 : 7- and -5 : 7-dimethyl-1-oxonaphthalene it was possible to isolate substances regarded as tetramethylbenzofluoranthenes from the by-products. But with 1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethyl-1-oxonaphthalene the cyclisation did not take place, the final by-product being a colourless αβ-unsaturated ketone, $C_{24}H_{26}O$, which did not lose water on further heating with polyphosphoric acid. Reduction of the carbonyl group by the Huang-Minlon procedure gave an unsaturated hydrocarbon, $C_{24}H_{28}$.

EXPERIMENTAL

Ring-closures.—1 : 2 : 3 : 4-*Tetrahydro*-5 : 7-*dimethyl*-1-*oxonaphthalene*. To a solution of phosphoric oxide (240 g.) in phosphoric acid (200 c.c.; *d* 1·75) at 160° (oil-bath) γ-2 : 4-dimethylphenylbutyric acid (60 g.) was added. This formed a layer above the "polyphosphoric acid" and, on vigorous stirring of the mixture with a thermometer, the temperature fell to 140° and then rose quickly; at 155° the melt became homogeneous. It was kept for 3 min. at 160° and the hot mixture was then poured into cold water. From the mixture ether extracted a red oil; on distillation there was obtained a main fraction of b. p. 113°/0·25 mm. (49·8 g., 92%) which crystallised immediately. A recrystallised specimen melted at 48·8° (thermometer in the liquid) and at 49—50° (capillary tube). The values in the literature vary from 47° to 50°. In a second experiment, in which the melt was kept for 3 min. at 174°, the yield was only 74%, and a brown syrup remained after distillation of the tetralone.

1 : 2 : 3 : 4-*Tetrahydro*-7-*methyl*-1-*oxonaphthalene*. Heating γ-*p*-tolylbutyric acid (80 g.) in polyphosphoric acid (phosphoric oxide, 240 g., and phosphoric acid, 267 c.c. of *d* 1·75) for 3 min. at 155° gave 64·7 g. (90% yield) of crystalline tetralone, m. p. 31°.

Similarly γ-phenylbutyric acid during 1—2 min. at 155° gave 80—90% yields, γ-*p*-tolylvaleric acid during 2·5 min. at 161° an 88% yield, and γ-2 : 5-dimethylphenylbutyric acid during 3 min. at 165° gave a 93% yield of the corresponding tetralones.

Action of Polyphosphoric Acid on α-Tetralone.—α-Tetralone (11·6 g.) was stirred with a solution of phosphoric oxide (58 g.) in syrupy phosphoric acid (39 c.c.; *d* 1·75) at 170° for 10 min. After the cooled mixture had been poured into water an ethereal extract of it was washed well with water and with sodium carbonate solution, then dried and distilled. Unchanged tetralone (7 g.) passed over at temperatures below 190°/0·03 mm., followed by 0·7 g. of yellow syrup, b. p. 190—200°/0·03 mm., leaving a high-boiling residue (2 g.). On an alumina column a light petroleum solution of the yellow syrup gave a colourless and also a yellow band. Elution with benzene gave, from the colourless band, 1 : 2 : 3 : 4 : 9 : 12 : 13 : 14-*octahydro*-10 : 11-*benzofluoranthene*, m. p. 145—148° (Found : C, 92·1; H, 7·2. $C_{20}H_{20}$ requires C, 92·2; H, 7·8%). From the other band yellow crystals of m. p. 160—162° were obtained and these, after attempted dehydrogenation (refluxing in *p*-cymene solution for 12 hr. with palladised charcoal), gave yellow crystals (from ethanol), m. p. 164° (Found : C, 95·6; H, 4·7. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·7%). The picrate, brick-red needles from ethanol, melted at 194—195° (Found: C, 65·1; H, 3·1. Calc. for $C_{20}H_{12},C_6H_3O_7N_3$: C, 64·9; H, 3·1%). Nenitzescu and Avram (*loc. cit.*) give for 10 : 11-benzofluoranthene, m. p. 165°, and for the brick-red picrate, m. p. 195°.

By-products of Cyclisation of Arylbutyric Acids.—(i) *From ring-closure of* γ-2 : 4-*dimethylphenylbutyric acid.* The brown syrup remaining from the distillation of the tetralone, on being rubbed with ether, gave a solid, m. p. 172—181°, most of which was sparingly soluble in boiling ethanol. After 6 crystallisations from benzene–ethanol it yielded a colourless 3 : 4 : 12 : 13-*tetrahydro*-(?)-*tetramethyl*-10 : 11-*benzofluoranthene*, m. p. 198—199° (Found : C, 92·6; H, 7·6%; *M*, in camphor, 272. $C_{24}H_{24}$ requires C, 92·2; H, 7·8%; *M*, 312). This hydrocarbon (0·3 g.), dehydrogenated for 4 hr. in refluxing *p*-cymene (6 c.c.) with palladised charcoal (0·2 g.), gave orange prisms of (?)*tetramethyl*-10 : 11-*benzofluoranthene*, m. p. 194° (Found : C, 93·0; H, 6·8. $C_{24}H_{20}$ requires C, 93·4; H, 6·6%). The *picrate*, ruby needles from *n*-propanol, was unstable and melted at *ca.* 190° (decomp.; rapid heating) (Found : C, 67·0; H, 4·4; N, 7·7. $C_{30}H_{23}O_7N_3$ requires C, 67·0; H, 4·3; N, 7·8%).

(ii) γ-*p*-Tolylvaleric acid with polyphosphoric acid at 161° (2·5 min.) gave an 88% yield of the tetralone and a small amount of a high-boiling residue. A benzene solution of this residue, chromatographed on alumina, gave a yellow *hydrocarbon* which, crystallised 4 times from ethanol, melted at 221—222° (Found : C, 90·9; H, 8·8. $C_{24}H_{28}$ requires C, 91·1; H, 8·9%). There was insufficient material for dehydrogenation.

(iii) γ-2 : 5-Dimethylphenylbutyric acid on ring-closure gave, besides the 93% yield of tetralone, a small amount of high-boiling residue from which, on crystallisation from ethanol–benzene, a colourless *substance*, m. p. 222·5°, was obtained (Found : C, 87·6; H, 8·0. $C_{24}H_{26}O$ requires C, 87·2; H, 7·9%). This was unsaturated towards dilute permanganate solution; it was recovered unchanged from heating to 160° with polyphosphoric acid; it gave complex derivatives with hydroxylamine hydrochloride and with 2 : 4-dinitrophenylhydrazine. But when heated with hydrazine hydrate and sodium hydroxide in ethylene glycol, for 4 hr. at 160°

and then for 5 hr. at 198°, it yielded a colourless *hydrocarbon*, m. p. 156—158° (Found: C, 91·1; H, 9·2. $C_{24}H_{28}$ requires C, 91·1; H, 8·9%).

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