73. *Isomerisation Reactions. Part III.*

By R. R. Aitken, G. M. Badger, and J. W. Cook.

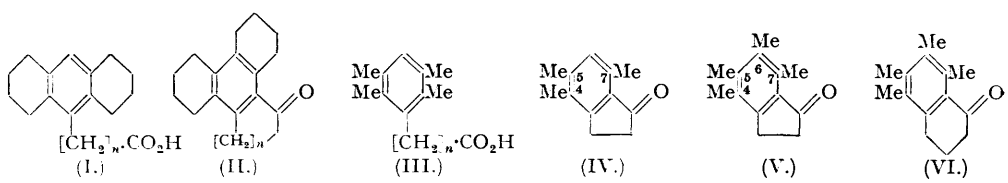
The action of hydrogen fluoride on a series of acids (III; n = 0, 1, 2, 3) derived from durene has been investigated. In two cases (n = 0 or 1) no reaction occurred. *β-Durylpropionic acid* (n = 2) gave a mixture of ketones (IV and V), one formed by elimination of a methyl group and the other by migration. *γ-Durylbutyric acid* (n = 3) gave 5 : 6 : 7 : 8-tetramethyl-1-tetralone (VI) by migration of methyl. *β-Pentamethylphenylpropionic acid* reacted with hydrogen fluoride to give (V), with elimination of methyl, whereas *γ-pentamethylphenylbutyric acid* gave no ketonic product.

Compounds of type (I), in which n = 2 or 3, undergo isomerisation and cyclisation on treatment with anhydrous hydrogen fluoride at room temperature, to give derivatives of *s*-octahydrophenanthrene (II) (Badger, Carruthers, Cook, and Schoental, *J.*, **1949**, 169; Badger, Carruthers, and Cook, *ibid.*, p. 2044). Cyclisation is evidently essential for isomerisation to occur, for hydrogen fluoride did not isomerise a number of related compounds in which the subsequent cyclisation could not take place. The analogy between this type of isomerisation and that observed with aluminium chloride has already been noted, as well as the analogy to the Jacobsen reaction, in which isomerisations are brought about by concentrated sulphuric acid. In these last two cases, however, cyclisation is not an essential feature, and in this respect, therefore, the isomerisations observed with hydrogen fluoride, at room temperature, appear to be unique. However, the displacement of an alkyl group by an entering acyl group in the preparation of aromatic ketones using aluminium chloride has been reported by Auwers and Mauss (*Annalen*, **1928**, **460**, 240), and by Hennion and McLeese (*J. Amer. Chem. Soc.*, **1942**, **64**, 2421).

Baddeley (*J.*, **1944**, 232) has pointed out that migrations of alkyl groups in benzene homologues, phenols, aryl ketones, and hydroxyaryl ketones by means of aluminium chloride are related to one another and to the Jacobsen reaction. He also distinguishes between two types of aluminium chloride isomerisations, namely (i) the reversible isomerisation of homologues of benzene and phenol associated with intramolecular migrations of alkyl groups to adjacent positions, and (ii) the irreversible isomerisation of aromatic ketones, closely comparable with the Jacobsen reaction, which involve intramolecular migration of alkyl groups to adjacent positions and, alternatively, migration, perhaps intramolecular, of acyl groups. The hydrogen fluoride rearrangements of octahydroanthracene derivatives show some of the features of both types. For this reason, and because most of the work on the Jacobsen reaction has been carried out with polyalkylbenzenes (" Organic Reactions," **1942**, Vol. I, p. 370), we have extended our studies with hydrogen fluoride to some derivatives of durene and of pentamethylbenzene.

Durene itself was unaffected by hydrogen fluoride at room temperature, a result which is in agreement with previous work (Calcott, Tinker, and Weinmayr, *J. Amer. Chem. Soc.*, **1939**, **61**, 1010), although it is known that hydrogen fluoride isomerises homologues of benzene at high temperatures and pressures (U.S.P. 2,416,184).

Similarly, durenecarboxylic acid and *durylacetic acid* (III; n = 1) were recovered unchanged after treatment with hydrogen fluoride, and in this respect, these results are entirely comparable with those observed in the case of octahydroanthracene and its simple derivatives (Badger, Carruthers, and Cook, *loc. cit.*). With *β-durylpropionic acid* (III; n = 2), and with *γ-durylbutyric acid* (III; n = 3), cyclisation and isomerisation were observed.



Treatment of β-durylpropionic acid with hydrogen fluoride gave a mixture from which 4 : 5 : 7-*trimethylindan*-1-*one* (IV) and 4 : 5 : 6 : 7-*tetramethylindan*-1-*one* (V) were isolated and characterised as the *oximes*. The former ketone is formed by simultaneous cyclisation with the *loss* of a methyl group, and the latter, formed in rather greater amount, by simultaneous cyclisation with *migration* of a methyl group. Similar effects have often been observed in isomerisations with other reagents such as aluminium chloride. The structures of the two ketones were established by oxidation with dilute nitric acid to the corresponding benzenepolycarboxylic acids. Cyclisation and isomerisation of γ-durylbutyric acid proceeded rather more readily, and in better yield, to give only one ketone. This ketone, also characterised as its *oxime*, was oxidised to mellitic acid, and was therefore 5 : 6 : 7 : 8-*tetramethyl*-1-*tetralone* (VI).

β-*Pentamethylphenylpropionic acid* on treatment with hydrogen fluoride gave only one ketone, namely 4 : 5 : 6 : 7-tetramethylindanone (V), formed by cyclisation with elimination of a methyl group. Unexpectedly, the homologous acid, γ-*pentamethylphenylbutyric acid* gave no ketonic product with hydrogen fluoride.

Durenecarboxylic acid was prepared from bromodurene by carboxylation of its magnesio-derivative (Fuson and Kelton, *J. Amer. Chem. Soc.*, 1941, **63**, 1500). Chloromethylation of durene, by a modification of the method used by Nauta and Dienske (*Rec. Trav. chim.*, 1936, **55**, 1000) for mesitylene, gave chloromethyldurene and *bischloromethyldurene*. The former, on interaction with potassium cyanide, followed by hydrolysis of the resulting *cyanomethyldurene*, gave durylacetic acid (III; $n = 1$). Condensation of chloromethyldurene with ethyl sodiomalonate gave *ethyl durylmethylmalonate*, which on hydrolysis to the *acid* followed by decarboxylation gave β-durylpropionic acid (III; $n = 2$). Chain lengthening by the Arndt–Eistert procedure gave, through the *amide*, γ-durylbutyric acid (III; $n = 3$). β-Pentamethylphenylpropionic acid and γ-pentamethylphenylbutyric acid were obtained from pentamethylbenzene by exactly similar routes. The former was also prepared by chloromethylation of β-durylpropionic acid followed by catalytic hydrogenation of the *chloromethyldurylpropionic acid* so formed.

The Friedel–Crafts reaction between durene and succinic anhydride in presence of aluminium chloride has also been investigated. In carbon disulphide solution this gave a mixture from which the normal product, γ-*keto*-γ-*durylbutyric acid*, m. p. 160°, was isolated with difficulty, together with the isomeric γ-*keto*-γ-*prehnitylbutyric acid*, m. p. 107°. Under these conditions Muhr (*Ber.*, 1895, **28**, 3217) claimed to have prepared γ-keto-γ-durylbutyric acid, m. p. 117°. This was evidently a mixture. When the reaction was carried out in tetrachloroethane solution γ-keto-γ-durylbutyric acid was more readily obtained pure, its isomer being formed in only small amount. This solvent influence is somewhat similar to that observed by Badger, Carruthers, and Cook (*loc. cit.*) in the corresponding reaction of *s*-octahydroanthracene and succinic anhydride. These authors found that in tetrachloroethane a mixture of keto-acids was formed, whereas the use of carbon disulphide led to more complete isomerisation to octahydrophenanthroylpropionic acid.

Reduction of γ-keto-γ-durylbutyric acid to γ-durylbutyric acid (III; $n = 3$) was difficult, presumably on account of steric hindrance. It was not effected by hydrazine hydrate at 195°, and although the Clemmensen method yielded a small amount of the desired acid much of the keto-acid was unchanged.

Experimental.

Durene.—Durene was prepared by bischloromethylation of technical xylene, followed by reduction of the bischloromethyl compound with zinc and sodium hydroxide solution (von Braun and Nelles, *Ber.*, 1934, **67**, 1094). Reduction by catalytic hydrogenation in acetone, over palladised asbestos, gave a theoretical yield in small-scale (2-g.) runs, but on a large scale the reduction was tediously long and tended to give incompletely reduced material. Durene was recovered unchanged after treatment, for 36 hours, with anhydrous hydrogen fluoride at room temperature.

Chloromethyldurene.—A mixture of durene (22 g.), glacial acetic acid (50 c.c.), concentrated hydrochloric acid (110 c.c.), and aqueous formaldehyde (40%; 10·7 g.) was heated at 70°, for 6 hours, a further quantity (4·4 g.) of formaldehyde being added after 3 hours. After cooling, the aqueous layer was decanted, and the solid dissolved in benzene, washed with sodium carbonate solution and then water, and dried (K_2CO_3). Distillation gave chloromethyldurene (22 g.), b. p. 139—141°/15 mm., which, after crystallisation from methanol, had m. p. 65—66° (Fuson and Sperati, *J. Amer. Chem. Soc.*, 1941, **63**, 2643, give m. p. 67—68°). The solid residue from the distillation was sublimed at 160°/15 mm. Recrystallisation of the sublimate (3—5 g. in different runs) from light petroleum gave *bischloromethyldurene* as colourless needles, m. p. 193—194° (Found: C, 62·0; H, 6·8; Cl, 30·5. $C_{12}H_{16}Cl_2$ requires C, 62·3; H, 7·0; Cl, 30·7%).

Ethyl β-Durylmethylmalonate.—A mixture of atomised sodium (3·5 g.), ethyl malonate (24·2 g.), and benzene (75 c.c.) was heated under reflux for 3 hours. While still warm, chloromethyldurene (25·2 g.) in benzene (40 c.c.) was added, and the whole heated under reflux for a further 2 hours. After cooling,

the mixture was poured into water, and the benzene layer separated, washed, and dried. Fractional distillation gave chloromethyldurene, ethyl malonate, and *ethyl β-durylmethylmalonate*, b. p. 158—160°/0·5 mm. (31 g.), which crystallised from light petroleum in colourless prisms, m. p. 58—59° (Found : C, 70·5; H, 8·6. $C_{18}H_{26}O_4$ requires C, 70·6; H, 8·6%). Hydrolysis with aqueous-ethanolic potassium hydroxide for 3 hours gave *β-durylmethylmalonic acid*, which crystallised from water as colourless plates, m. p. 176° (with evolution of carbon dioxide) (Found : C, 67·4; H, 6·9. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%).

β-Durylpropionic Acid (III; $n = 2$).—The above malonic acid (2 g.) was heated in an oil-bath at 180°, until evolution of gas ceased. *β-Durylpropionic acid* (1·5 g.) formed needles, m. p. 170°, from benzene or aqueous acetic acid (Found : C, 75·6; H, 8·6. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%). *β-Durylpropionamide* crystallised from ethanol in needles, m. p. 201—202° (Found : C, 76·2; H, 9·0; N, 7·0. $C_{13}H_{19}ON$ requires C, 76·1; H, 9·3; N, 6·8%).

Isomerisation and Cyclisation of β-Durylpropionic Acid.—The above acid (2 g.) was allowed to stand with excess of anhydrous hydrogen fluoride for 36 hours. The resulting dark residue was poured on ice and extracted with ether. Extraction of the ethereal solution with dilute sodium carbonate solution, followed by acidification of the extract, gave unchanged acid (1·4 g.) identified by m. p. and mixed m. p. The ethereal solution yielded a brown oil (0·5 g.), which solidified when kept. After purification by passage of its solution in benzene through a column of alumina, the product was obtained as a pale yellow solid which separated from light petroleum as a mixture of ketone-A (needles) and ketone-B (prisms), which were separated mechanically.

Purification of ketone-A by recrystallisation from light petroleum, gave 4 : 5 : 7-*trimethylindan*-1-*one* (IV) as colourless needles, m. p. 104—105° [Found : C, 82·5; H, 8·1%; *M* (Rast), 199. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%; *M*, 174]. The *oxime* formed colourless plates, m. p. 223—224° (decomp.), from benzene–light petroleum (Found : C, 76·3; H, 7·8; N, 7·35. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0; N, 7·4%). Hydrolysis of the oxime with dilute hydrochloric acid in boiling ethanol regenerated the ketone, of unchanged m. p. For oxidation, the ketone (0·12 g.) was heated at 175—180° in a sealed tube, for 6 hours, with water (2 c.c.) and concentrated nitric acid (1 c.c.). Evaporation to dryness and esterification of the residue with excess of ethereal diazomethane gave methyl benzenepentacarboxylate, m. p. 145—146°, not depressed on admixture with an authentic specimen prepared in a similar manner by oxidation of pentamethylbenzene (*cf.* Cook and Hewett, *J.*, 1934, 371; Fieser and Joshel, *J. Amer. Chem. Soc.*, 1940, **62**, 1213).

Purification of ketone-B by recrystallisation from light petroleum (charcoal) gave 4 : 5 : 6 : 7-*tetramethylindan*-1-*one* (V) as colourless plates, m. p. 149—150° [Found : C, 82·8; H, 8·6%; *M* (Rast), 172. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%; *M*, 188]. The m. p. was unchanged when the ketone was purified through its *oxime*, which crystallised from ethanol in small needles, m. p. 211—213° (Found : C, 77·0; H, 8·4; N, 7·2. $C_{13}H_{17}ON$ requires C, 76·8; H, 8·4; N, 6·9%). Oxidation of tetramethylindanone with dilute nitric acid, as described above for trimethylindanone, gave methyl mellitate, m. p. 186—187°, from methanol, not depressed by admixture with an authentic specimen, m. p. 187—188°.

γ-Keto-γ-duryl- and γ-Keto-γ-prehnityl-butyric Acid.—To a stirred ice-cold suspension of aluminium chloride (10 g.) in carbon disulphide (30 c.c.), a solution of durene (3·3 g.) and succinic anhydride (2·5 g.) in carbon disulphide (50 c.c.) was added dropwise, during 30 minutes. After being stirred for 4 hours at 0° and then 8 hours at room temperature, the mixture was set aside, without stirring, for a further 16 hours. The acidic product (3·2 g.) had m. p. 117—134°, and was purified by crystallisation from ethanol, followed by crystallisation of the sodium salt from water. *γ-Keto-γ-durylbutyric acid*, obtained from the purified sodium salt, formed colourless prisms, m. p. 160—161°, from ethanol (Found : C, 71·5; H, 8·0. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). Durene was regenerated when this acid was heated with concentrated hydrochloric acid in a sealed tube at 150° for 6 hours. The p-*nitrobenzyl* ester crystallised from methanol in plates, m. p. 120—121° (Found : C, 68·3; H, 6·4; N, 3·5. $C_{21}H_{23}O_5N$ requires C, 68·3; H, 6·3; N, 3·8%).

The same acid was isolated following interaction of durene and succinic anhydride with aluminium chloride, in tetrachloroethane solution.

The acid recovered from the mother-liquors of the sodium salt was crystallised from aqueous ethanol and then benzene–hexane, and gave *γ-keto-γ-prehnitylbutyric acid*, m. p. 107—108° (Found : C, 71·6; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). This acid (0·1 g.) was added to ice-cold 10% sodium hypobromite solution (10 c.c.), and the suspension gradually heated to 100°, with occasional shaking (2 hours). The mixture was maintained at 100° for 3 hours and filtered hot. Acidification gave prehnitenecarboxylic acid, m. p. 165—166°, from ligroin (lit., m. p. 168—169°), and the amide prepared from it had m. p. 220° (lit., m. p. 222°).

γ-Durylbutyric Acid (III; $n = 3$).—(*a*) A mixture of β-durylpropionic acid (III; $n = 2$) (2 g.), thionyl chloride (2·5 c.c.), benzene (15 c.c.), and pyridine (1 drop) was refluxed for 2 hours. The benzene and excess of thionyl chloride were then removed in a vacuum, and the residue was evaporated with two portions (10 c.c. each) of benzene. The residue was then dissolved in benzene (20 c.c.) and added gradually, with stirring, to an ice-cold solution of diazomethane (from 7 g. of nitrosomethylurea) in ether (120 c.c.). The resulting solution was evaporated to dryness in a stream of dry air, and the residue, in dioxan (20 c.c.), was refluxed for 2½ hours with a solution of 10% silver nitrate (3 c.c.) and 20% ammonia (15 c.c.). The resulting mixture was filtered hot, the residue on the paper was washed with hot dioxan, and the combined solutions were poured into water. *γ-Durylbutyramide* (1·05 g.) crystallised from ethanol in colourless plates, m. p. 171—172° (Found : C, 76·8; H, 9·5; N, 6·1. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·7; N, 6·4%). Hydrolysis of the amide (1 g.) was effected by 10 hours' refluxing with potassium hydroxide (5 g.) in ethanol (50 c.c.). *γ-Durylbutyric acid* (III; $n = 3$) (0·89 g.) crystallised from benzene, and then from *cyclo*hexane, in colourless plates, m. p. 139—140° (Found : C, 76·2; H, 9·0. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%).

(*b*) An attempt to prepare durylbutyric acid by reduction of γ-keto-γ-durylbutyric acid by the modified Kishner–Wolff procedure (Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487) was unsuccessful, only unchanged material being isolated. Reduction by the Clemmensen method was, however, partly successful. A mixture of γ-keto-γ-durylbutyric acid (1·5 g.), toluene (15 c.c.), acetic acid (10 c.c.),

concentrated hydrochloric acid (75 c.c.), and amalgamated zinc (10 g.) was refluxed for 48 hours. Additions of zinc (total, 15 g.) and of hydrochloric acid (total, 75 c.c.) were made at intervals. The product, m. p. 114—130°, was purified by conversion into the sodium salt, and separation into soluble and sparingly soluble fractions. Acidification of the sparingly soluble salt gave unchanged keto-acid (1·0 g.), identified by m. p. and mixed m. p. Acidification of the soluble salt, followed by recrystallisation of the product from *cyclo*hexane, gave γ-durylbutyric acid (0·27 g.), m. p. 138—139°, identical with that obtained as under (*a*).

Isomerisation and Cyclisation of γ-Durylbutyric Acid (III; $n = 3$).—γ-Durylbutyric acid (1 g.) was set aside in excess of anhydrous hydrogen fluoride for 36 hours. The resulting brown residue was poured on ice and extracted with ether. Extraction of the ethereal solution with dilute sodium carbonate solution, followed by acidification of the extract, gave unchanged acid (0·38 g.), identified by m. p. and mixed m. p. Evaporation of the ethereal solution gave a slightly coloured solid residue which on crystallisation from ethanol (twice) gave 5 : 6 : 7 : 8-*tetramethyl*-1-*tetralone* (VI) as colourless needles, m. p. 106—107° [Found : C, 83·4; H, 9·2%; *M* (Rast), 200. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%; *M*, 202]. The *oxime* formed colourless needles, m. p. 185—186°, from ethanol (Found : C, 77·15; H, 8·8; N, 6·6. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8; N, 6·45%). The oxime (0·05 g.), hydrolysed as described above for trimethylindanone, yielded after crystallisation from ethanol the ketone of the same m. p. Oxidation of this ketone (VI) with dilute nitric acid as described above for trimethylindanone yielded methyl mellitate, m. p. 185—187°, from methanol, not depressed on admixture with an authentic specimen.

Durenecarboxylic Acid.—This was obtained from the bromo-derivative by interaction with magnesium in dry ether, followed by carboxylation with solid carbon dioxide. It crystallised from light petroleum in colourless plates, m. p. 178°. Fuson and Kelton (*J. Amer. Chem. Soc.*, 1941, **63**, 1500) give m. p. 179—180°. It was recovered unchanged after being kept in anhydrous hydrogen fluoride, at room temperature, for 48 hours.

Durylacetic Acid.—Potassium cyanide (5 g.) in water (9 c.c.) was added to chloromethyldurene (2 g.) in ethanol (25 c.c.), and the mixture was boiled under reflux for 2 hours. The cooled solution was added to a large excess of water. The precipitated *cyanomethyldurene* formed needles, m. p. 84—85° (from aqueous methanol), after distillation (b. p. 168°/20 mm.) (Found : C, 83·3; H, 8·5; N, 8·3. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%). Hydrolysis of the crude cyanide, by boiling with a mixture of equal volumes of sulphuric acid, water, and acetic acid, gave *durylacetic acid* which crystallised from benzene in colourless plates, m. p. 198—199° (Found : C, 75·2; H, 8·1. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%). Durylacetic acid was recovered unchanged after treatment with hydrogen fluoride, at room temperature, for 48 hours.

Pentamethylbenzene.—Pentamethylbenzene was prepared by bischloromethylation of mesitylene (Nauta and Dienske, *Rec. Trav. chim.*, 1936, **55**, 1000), followed by reduction of the bischloromethyl compound. Several methods were investigated in an attempt to accomplish this reaction. Reduction by catalytic hydrogenation with palladised asbestos in acetone, though efficient in small scale runs (2 g.) as with dichloromethylxylene, was found to be tediously long and to give incompletely reduced products. Reduction with zinc and aqueous alcohol (*cf.* Hewett, *J.*, 1940, 298) gave mainly non-crystalline undistillable products, as did reduction with nickel–aluminium alloy and aqueous sodium hydroxide, at about 90°. The reduction was most readily accomplished by stirring the bischloromethylmesitylene, in toluene, with zinc and aqueous sodium hydroxide. When benzene was used in place of toluene, as described by von Braun and Nelles (*Ber.*, 1934, **67**, 1094) for the reduction of bischloromethylxylene, the yield of pentamethylbenzene was considerably reduced.

Pentamethylbenzene was also obtained by shaking chloromethyldurene (10 g.) in acetone (150 c.c.) with hydrogen at ordinary pressures and temperatures in presence of palladium on asbestos as catalyst. Reduction was complete within 3¾ hours.

Pentamethylchloromethylbenzene.—A mixture of pentamethylbenzene (14 g.), concentrated hydrochloric acid (70 c.c.), and aqueous formaldehyde (7 g.; 40%) was stirred while being heated at 65° for 6 hours, a further quantity (2·5 g.) of formaldehyde being added after 3 hours. After cooling, the aqueous layer was decanted and the semi-solid residue dissolved in benzene, washed with sodium carbonate solution and then with water, and dried (K_2CO_3). Distillation yielded *pentamethylchloromethylbenzene* (12 g.), b. p. 148°/14 mm., which crystallised from light petroleum in prisms, m. p. 82—84° (Found : C, 73·05; H, 8·8; Cl, 17·9. $C_{12}H_{17}Cl$ requires C, 73·3; H, 8·7; Cl, 18·0%). Pentamethylchloromethylbenzene was also obtained, though mixed with hexamethylbenzene, by treating hexamethylbenzene with phosphorus pentachloride as described by Jacobsen (*Ber.*, 1889, **22**, 1217), who claims to have obtained pentamethylchloromethylbenzene, m. p. 99°, by this method.

Ethyl Pentamethylbenzylmalonate.—A mixture of atomised sodium (1·7 g.), ethyl malonate (11·6 g.), and benzene (50 c.c.) was heated under reflux for 3 hours. Whilst still warm, pentamethylchloromethylbenzene (12 g.) in benzene (20 c.c.) was added, and the whole heated under reflux for a further 2 hours. The cooled mixture was then poured into water, and the benzene layer separated, washed, and dried. Distillation gave *ethyl pentamethylbenzylmalonate*, b. p. 177—180°/1·5 mm. (14·5 g.), which crystallised from ethanol in needles, m. p. 71—73° (Found : C, 71·2; H, 8·9. $C_{19}H_{28}O_4$ requires C, 71·2; H, 8·8%). Hydrolysis of the ester (14·5 g.) with aqueous-ethanolic potassium hydroxide for 2 hours gave *pentamethylbenzylmalonic acid* (9·4 g.), which formed plates, m. p. 191·5° (with evolution of carbon dioxide), from aqueous ethanol (3 : 1) (Found : C, 68·45; H, 7·8. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%).

β-Pentamethylphenylpropionic Acid.—The malonic acid (9·4 g.) was heated in an oil-bath at 195° till evolution of gas had ceased. *β-Pentamethylphenylpropionic acid* (6·4 g.) formed needles, m. p. 175—176°, from benzene (Found : C, 76·2; H, 9·3. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%).

This acid was also obtained as follows. A mixture of β-durylpropionic acid (2 g.), aqueous formaldehyde (1·5 g.; 40%), and concentrated hydrochloric acid (20 c.c.) was stirred for 6 hours whilst being heated at 60°. After 3 hours a further quantity (1·0 g.) of formaldehyde was added. The cooled mixture was added to water and filtered. *β-Chloromethyldurylpropionic acid* formed needles, m. p. 216—218°, from dioxan (Found : C, 66·2; H, 7·45; Cl, 14·1. $C_{14}H_{19}O_2Cl$ requires C, 66·0; H, 7·5; Cl, 13·9%).

β-Acetoxymethyldurylpropionic acid, prepared from this by warming it with sodium acetate in acetic acid to 100° for 30 minutes, formed long fine needles, m. p. 203—204°, from aqueous acetic acid (Found: C, 69·0; H, 8·0. $C_{16}H_{22}O_4$ requires C, 69·0; H, 8·0%). *β-Hydroxymethyldurylpropionic acid*, prepared by sodium carbonate hydrolysis of either of the above two acids, formed large firm needles, m. p. 213—214° with evolution of gas (from ethyl acetate) (Found: C, 71·4; H, 8·4. $C_{14}H_{20}O_3$ requires C, 71·15; H, 8·5%).

One run of the chloromethylation reaction, when acetic acid was present, yielded β-acetoxymethyldurylpropionic acid; its identity was shown by m. p. and mixed m. p. with a specimen prepared as described above and by hydrolysis with sodium carbonate to β-hydroxymethyldurylpropionic acid.

Chloromethyldurylpropionic acid (0·3 g.) in acetone (15 c.c.) was shaken with hydrogen at ordinary temperature and pressure in presence of palladium-black. Reduction was complete in 2 hours. The filtered residue yielded β-pentamethylphenylpropionic acid, m. p. 172—174°, not depressed by mixture with the specimen prepared as described above.

Isomerisation and Cyclisation of β-Pentamethylphenylpropionic Acid.—The acid (1 g.) was left in contact with excess of anhydrous hydrogen fluoride for 36 hours. The resulting brown oil was poured on ice and extracted with ether. Extraction of the ethereal solution with sodium carbonate solution followed by acidification of the alkaline extract gave unchanged acid (0·37 g.). The ethereal solution yielded a brown oil (0·54 g.) which solidified in an ice-bath. After purification by passage of its benzene solution through a column of alumina the product, a pale yellow solid, was crystallised from light petroleum. It formed plates, m. p. 150—152°, not depressed by admixture with tetramethylindanone (V). Identification was completed by preparation of the oxime, m. p. 213—214°.

γ-Pentamethylphenylbutyric Acid.—A mixture of β-pentamethylphenylpropionic acid (2·2 g.), thionyl chloride (2·75 c.c.), benzene (15 c.c.), and pyridine (1 drop) was refluxed for 2 hours. The benzene and excess of thionyl chloride were removed *in vacuo*, and the residue was evaporated with 2 portions (10 c.c. each) of dry benzene. The residue in benzene (20 c.c.) was added with stirring to an ice-cold solution of diazomethane (from 8 g. of nitrosomethylurea) in ether (150 c.c.). The resulting mixture, from which part of the diazoketone could be crystallised by cooling it in ice, was evaporated to dryness in a stream of dry air, and the residue, dissolved in dioxan (25 c.c.), was refluxed for 2½ hours with a solution of silver nitrate (3 c.c.; 10%) and ammonia (15 c.c.; 20%). The resulting mixture was filtered hot, the residue on the paper was washed with hot ethanol, and the combined solutions were poured into water. *γ-Pentamethylphenylbutyramide* (1·15 g.) formed very small needles, m. p. 185—186°, from benzene (Found: C, 77·4; H, 10·2; N, 6·4. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9; N, 6·0%). Hydrolysis of the amide (1·15 g.) was effected by refluxing it for 10 hours with potassium hydroxide (5 g.) in ethanol (50 c.c.). *γ-Pentamethylphenylbutyric acid* (0·75 g.) formed plates, m. p. 157—158°, from benzene (Found: C, 76·8; H, 9·4. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). When this acid was left in contact with excess of hydrogen fluoride for 36 hours it was recovered entirely unchanged.

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UNIVERSITY OF GLASGOW. [*Received, October 26th*, 1949.]