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1,2,3,5- and 1,2,3,8-Tetramethylnaphthalene

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1,2,3,5- and 1,2,3,8-Tetramethylnaphthalene have been synthesised from β -(3,4,5-trimethylbenzoyl)propionic acid.

AUTHENTIC 1,2,3,5-tetramethylnaphthalene was required in connection with degradative work on compound Y from *Leonotis leonurus*.¹ Since the intermediates were available the 1,2,3,8-isomer was also prepared; neither has been described before. Seventeen of the twentytwo tetramethylnaphthalenes are now known; twelve are recorded in Donaldson's book² while the 1,2,3,6-,³ 1,2,4,6-,^{4,5} and 1,3,6,7-isomers ³ have also been made.

The starting material, β -(3,4,5-trimethylbenzoyl)propionic acid, was prepared from 1,2,3-trimethylbenzene and succinic anhydride by Tucker et al.⁶ That it is not the 2,3,4-trimethyl analogue, as previously thought, was shown by oxidation with permanganate to benzene-1,2,3,5-tetracarboxylic acid. β -(3,4,5-Trimethylbenzoyl)propionic acid was converted successively by



Ultraviolet absorption curves for 1,2,3,5-tetramethylnaphthalene (---) and 1,2,3,8-tetramethylnaphthalene (-

Clemmensen reduction, ring closure, reaction with methyl-lithium,⁷ and dehydrogenation into 1,2,3,8tetramethylnaphthalene.

Ethyl β -(3,4,5-trimethylbenzoyl) propionate was treated with 1.5 mol. of methylmagnesium bromide and the solution refluxed for several hours to hydrolyse the intermediate unsaturated ester to the acid.⁸ The latter was hydrogenated, cyclised, reduced, and dehydro-

D. E. A. Rivett, J. Chem. Soc., 1964, 1857.
N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds," Edward Arnold Ltd., London, 1958.
B. A. Arbusov and A. R. Wil'chinskaya, Zhur. obshchei

Khim., 1961, 31, 2199 (Chem. Abs., 1962, 56, 4692).

genated to 1,2,3,5-tetramethylnaphthalene. The intermediate ketone failed to react with methyl-lithium in ether or boiling tetrahydrofuran and could thus not be converted into the unknown 1,2,3,5,8-pentamethylnaphthalene.

The ultraviolet absorption spectra of the two new tetramethylnaphthalenes are given in the Figure.

EXPERIMENTAL

Melting points are uncorrected and ultraviolet spectra were measured in 96% ethanol (λ in m μ).

β-(3,4,5-Trimethylbenzoyl)propionic Acid.—An ice-cooled solution of 1,2,3-trimethylbenzene (40.0 g., 0.33 mole) and succinic anhydride (38 g., 0.38 mole) in chlorobenzene (250 ml.) was treated with aluminium chloride (100 g., 0.75 ml.)mole). The mixture was stirred for 4 hr. at room temperature and left overnight. Ice and concentrated hydrochloric acid (150 ml.) were added and the chlorobenzene removed by steam-distillation. The crude acid was filtered off from the cool solution, purified by precipitation from aqueous sodium carbonate, and dried in a vacuum desiccator. Recrystallisation from benzene (200 ml.) afforded β -(3,4,5-trimethylbenzoyl)propionic acid (45.4 g., 62%), m. p. 147-149° (lit.,6 142-145°) (Found: Equiv., 222. Calc. for C₁₃H₁₆O₃: Equiv., 220).

Oxidation of β -(3,4,5-trimethylbenzoyl) propionic Acid to Benzene-1,2,3,5-tetracarboxylic Acid.—A solution of β -(3,4,5-trimethylbenzoyl)propionic acid (0.75 g.) and potassium hydroxide (1.0 g.) in water (10 ml.) was gently refluxed in a glycerol bath and a solution of potassium permanganate (6.5 g.) in water (100 ml.) added during 3 hr. The mixture was refluxed overnight. Unchanged permanganate was destroyed by the addition of a little ethanol, the hot solution filtered, and the precipitate washed well with hot water. The filtrate was acidified with concentrated hydrochloric acid, concentrated to 80 ml. under reduced pressure, and extracted continuously with ether for 3 hr. The solid (1.24 g.) remaining on evaporation of the solvent was refluxed with concentrated nitric acid (10 ml.) for $1\frac{1}{2}$ hr. to destroy the oxalic acid present. The clear solution was cooled in ice, the crystals (0.34 g.) filtered off, washed with a little ice-cold concentrated nitric acid, and dried in a vacuum desiccator (KOH) overnight. Esterification with diazomethane in ether-methanol and crystallisation from methanol (6 ml.) afforded methyl benzene-1,2,3,5-tetracarboxylate (0.30 g.), m. p. 109-110.5°, undepressed on admixture with authentic material, m. p. 110-112°, and possessing the same infrared spectrum.

⁴ S. Bory and P. Dietrich, Bull. Soc. chim. France, 1957, 228.
⁵ M. Stoll and M. Hinder, U.S.P. 2,802,880/1957 (Chem. Abs.,

1958, 52, 7357). ⁶ S. H. Tucker, M. Whalley, and J. Forrest, J. Chem. Soc., 1949, 3194.

Johnston, S. Searles, and Wen-chung Lin, J. Org. 7 G. D. Chem., 1962, 27, 4031.

⁸ W. T. G. Johnston, J. C. Smith, and C. M. Staveley, Chem. and Ind., 1954, 607.

1,2,3,8-Tetramethylnaphthalene.---A solution of 1,2,3,4tetrahydro-1-oxo-6,7,8-trimethylnaphthalene 6 (2.2 g., 0.011 mole) in dry ether (25 ml.) was added with stirring to a solution of methyl-lithium in ether (40 ml.), prepared under nitrogen from lithium (0.8 g., 0.11 mole) and methyl iodide (10 ml.). The mixture was stirred for 1 hr., left overnight, decomposed with dilute hydrochloric acid, and extracted with ether. The ether extract was dried and evaporated to give a brown oil (2.4 g) which showed only a very weak band at 6.0μ due to unchanged ketone. The crude alcohol (2.4 g.) was heated with 10% palladium charcoal catalyst at $290-310^{\circ}$ for $1\frac{1}{2}$ hr. The product was extracted with hexane, and the hexane solution passed through a column of alumina. 1,2,3,8-Tetramethylnaphthalene (0.85g., 40%) in the eluate was purified through its 1,3,5-trinitrobenzene complex and crystallised from methanol to give plates, m. p. 72° (Found: C, 91.0; H, 8.35. $C_{14}H_{16}$ requires \bar{C} , 91.25; H, 8.75%), $\lambda_{max.}$ 234 (ϵ 83,500), 282 (ε 5400), 290 (ε 5900).

The 1,3,5-trinitrobenzene complex formed fine yellow needles (from ethanol), m. p. 161–162° (Found: C, 60·2; H, 5·0; N, 10·8. $C_{20}H_{19}O_6N_3$ requires C, 60·4; H, 4·8; N, 10·6%). The trinitrotoluene complex formed fine yellow needles (from ethanol), m. p. 96° (Found: C, 61·8; H, 5·0; N, 10·3. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1; N, 10·2%). The picrate formed scarlet needles (from ethanol), m. p. 142° (Found: C, 58·4; H, 5·0; N, 10·5. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6; N, 10·2%).

Ethyl β-(3,4,5-Trimethylbenzoyl)propionate.—A solution of β-(3,4,5-trimethylbenzoyl)propionic acid (24·0 g.) in absolute ethanol (150 ml.) and concentrated sulphuric acid (20 ml.) was refluxed for 9 hr. and poured into water. The ester (26·1 g., 96%), extracted with ether, had m. p. 45·5—46·5°; a sample distilled at 135°/0·2 mm. was analysed (Found: C, 72·5; H, 8·0. $C_{15}H_{20}O_3$ requires C, 72·5; H, 8·1%). The semicarbazone crystallised from ethanol in long needles, m. p. 158—159° (Found: C, 62·5; H, 7·2; N, 14·1. $C_{16}H_{23}O_3N_3$ requires C, 62·9; H, 7·6; N, 13·8%).

 γ -Methyl- γ -(3,4,5-trimethylphenyl)butyric Acid.—A solution of methylmagnesium iodide, from magnesium (4.0 g., 0.165 mole) and methyl iodide (11.0 ml.) in ether (60 ml.), was added dropwise with vigorous stirring during $\frac{1}{2}$ hr. to a solution of ethyl β -(3,4,5-trimethylbenzoyl)propionate (26.1 g., 0.105 mole). The mixture was stirred under gentle reflux for 4 hr., whereupon the straw yellow precipitate which had formed was converted into a semi-viscous mass. and left overnight. The mixture was decomposed with ice and dilute hydrochloric acid and the red ether layer extracted several times with dilute sodium carbonate. The combined aqueous solutions were acidified with dilute hydrochloric acid, extracted thoroughly with ether, the ether extracts dried (Na₂SO₄) and evaporated to give a light brown oil (12.5 g.) which was distilled (bath-temp. 130- $150^{\circ}/0.0001$ mm.) to afford unsaturated acid (9.4 g.) which crystallised partly on standing. This acid was hydrogenated in acetic acid (100 ml.) over platinum oxide (0.5 g.) at 50 atm. for 7 hr. and the product dissolved in hexane (15 ml.). After a week at 5° crystals of γ -methyl- γ -(3,4,5-trimethylbenzoyl)propionic acid (5.6 g., 24% overall), m. p. 83—86°, were filtered off. Crystallisation was very slow. Recrystallisation from the same solvent afforded a pure sample, m. p. 89.5—90.5° (Found: C, 76.3; H, 9.1%; Equiv., 224. C₁₄H₂₀O₂ requires C, 76.3; H, 9.1%; Equiv., 220).

1,2,3,4-Tetrahydro-1-oxo-4,6,7,8-tetramethylnaphthalene.— The above acid (5.0 g.) was heated with 80% sulphuric acid (50 ml.) on a boiling-water bath with frequent shaking for $2\frac{1}{2}$ hr., the mixture poured into water, and extracted with ether. Unchanged acid was removed by shaking the ether solution with 10% sodium hydroxide, the ether solution dried (Na₂SO₄) and evaporated, and the residue distilled at 0.1 mm. (bath-temp. 90—110°) to afford an oil (4.3 g., 94%) which solidfied, m. p. 34—36°. An analytical sample of the 1,2,3,4-tetrahydro-1-oxo-4,6,7,8-tetramethylnaphthalene, prepared by crystallisation from methanol, had m. p. 39—40° (Found: C, 83.3; H, 8.9. C₁₄H₁₈O requires C, 83.1; H, 9.0%).

The 2,4-dinitrophenylhydrazone formed fine scarlet needles (from ethyl acetate), m. p. 199–200° (Found: C, 62.9; H, 6.0; N, 14.5. $C_{20}H_{22}O_4N_4$ requires C, 62.8; H, 5.8; N, 14.6%).

1,2,3,5-Tetramethylnaphthalene.-To amalgamated zinc [from granulated zinc (8 g.) kept for 15 min. in mercuric chloride (0.8 g.) in water (15 ml.) and concentrated hydrochloric acid (0.5 ml.)] was added in order, water (5 ml.), concentrated hydrochloric acid (12 ml.), and a solution of 1,2,3,4-tetrahydro-1-oxo-4,6,7,8-tetramethylnaphthalene $(2 \cdot 1 \text{ g.})$ in toluene (6 ml.). The mixture was refluxed vigorously for 40 hr., concentrated hydrochloric acid $(2 \times 10 \text{ ml.})$ being added after 10 and 20 hr. Water and ether were added, and the ether solution was washed with 10% sodium hydroxide and evaporated. The residue (2.1)g.) was heated with 10% palladium-charcoal at 290-310° for $1\frac{1}{2}$ hr. The product was extracted with hexane and the hexane solution passed through a column of alumina. Removal of the solvent afforded crude 1,2,3,5-tetramethylnaphthalene (1.7 g.), m. p. 42-44°, which was purified through the 1,3,5-trinitrobenzene complex and crystallised from methanol as fine needles (1.4 g., 74%), m. p. 54.5-55.5° (Found: C, 90.9; H, 8.5. C₁₄H₁₆ requires C, 91.25; H, 8.75%), λ_{max} 233 (ϵ 95,000), 280 (ϵ 5900), 290 (ϵ 6900). The 1,3,5-trinitrobenzene complex formed fine yellow needles (from ethanol), m. p. 181-182° (Found: C, 60.4; H, 4.9; N, 11.0. $C_{20}H_{19}O_6N_3$ requires C, 60.4; H, 4.8; N, 10.6%). The trinitrotoluene complex formed fine yellow needles (from ethanol), m. p. 106-107° (Found: C, 61.0; H, 5.2; N, 9.85. C₂₁H₂₁O₆N₃ requires C, 61.3; H, 5.1; N, 10.2%). The picrate formed scarlet needles (from ethanol), m. p. 165-166° (Found: C, 58.4; H, 4.6; N, 10.3. C₂₀H₁₉O₇N₃ requires C, 58.1; H, 4.6; N, 10.2%).

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