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SYNTHESIS OF 2- OR 4,6-DINITRO-*sec*-PENTYL PHENOLS

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In previous papers we have reported the synthesis and characterization of dinitro-*n*-alkyl and iso-alkyl phenols (1-3), compounds which have insecticidal and selective herbicidal properties. In view of the known superiority of 2,4-dinitro-6-*sec*-butyl phenol compared to the *n*-isomer (4, 5) it was of interest to prepare the *sec*-pentyl derivatives for physiological tests which will be reported elsewhere.

The isomeric *sec*-pentyl phenols were prepared by reacting a carbonyl compound with a

TABLE I
 Properties of alcohols and derived alkenes

| | Alcohols (C ₁₂ H ₁₈ O ₂) | | Alkenes (C ₁₂ H ₁₆ O) | | Nitrosyl chloride (9, 10) (C ₁₂ H ₁₆ NO ₂ Cl), melting point, °C |
|---|--|-------------------------------------|---|-------------------------------------|--|
| | Boiling point °C (mm) | <i>n</i> _D ²⁵ | Boiling point °C (mm) | <i>n</i> _D ²⁵ | |
| 2-(2-Methoxyphenyl)-pentanol-2 | 85 (0.02) | 1.5129 | 67 (0.4) | 1.5229 | 93 |
| 2-(4-Methoxyphenyl)-pentanol-2 | 100 (0.05) | 1.5308 | 70 (0.1) | 1.5370 | 84 |
| 3-(2-Methoxyphenyl)-pentanol-3 | 76 (0.01) | 1.5160 | 70 (0.03) | 1.5220 | 97 |
| 3-(4-Methoxyphenyl)-pentanol-3 (12, 13) | 87 (0.01) | 1.5278 | 58 (0.03) | 1.5310 | 79 |
| 2-(2-Methoxyphenyl)-3-methyl- butanol-2 (14) | 68 (0.02) | 1.5163 | 55 (0.1) | 1.5204 | — |
| 2-(4-Methoxyphenyl)-3-methyl- butanol-2 | 107 (0.02) | 1.5223 | 65 (0.1) | 1.5310 | — |

TABLE II
Properties of alkylanisoles and their derivatives

| | Alkylanisole (C ₁₂ H ₁₈ O) | | Sulphonamide (11) C ₁₂ H ₁₉ NO ₃ S, melting point, °C |
|------------------------------------|--|-------------------------------------|--|
| | Boiling point °C (mm) | <i>n</i> _D ²⁵ | |
| 2-(2-Methoxyphenyl)-pentane | 62 (0.3) | 1.4980 | 60 |
| 2-(4-Methoxyphenyl)-pentane | 68 (0.3) | 1.4970 | 63 |
| 3-(2-Methoxyphenyl)-pentane | 50 (0.01) | 1.5010 | — |
| 3-(4-Methoxyphenyl)-pentane (13) | 56 (0.02) | 1.5030 | 107 |
| 2-(2-Methoxyphenyl)-2-methylbutane | 58 (0.3) | 1.5070 | 111 |
| 2-(4-Methoxyphenyl)-2-methylbutane | 71 (0.5) | 1.5011 | 104 |

TABLE III
Properties of alkylphenols and their derivatives

| | Alkylphenol (C ₁₁ H ₁₆ O) | | 3,5-Dinitro- benzoate (C ₁₃ H ₁₈ N ₂ O ₆), melting point, °C | Dinitro-alkylphenol (C ₁₁ H ₁₄ N ₂ O ₆) | |
|------------------------------------|---|-------------------------------------|---|---|-------------------------------------|
| | Boiling point °C (mm) | <i>n</i> _D ²⁵ | | Boiling point °C (mm) | <i>n</i> _D ²⁵ |
| 2-(2-Hydroxyphenyl)-pentane | 65 (0.1) | 1.5122 | 85 | 145 (0.05) | 1.5686 |
| 2-(4-Hydroxyphenyl)-pentane (15) | 84 (0.5) | 1.5132 | 81 | 155 (0.1) | 1.5624 |
| 3-(2-Hydroxyphenyl)-pentane | 61 (0.1) | m.p. 64° | 87 | 138 (0.01) | 1.5668 |
| 3-(4-Hydroxyphenyl)-pentane | 83 (0.3) | m.p. 72° | 92 | 149 (0.03) | 1.5664 |
| 2-(2-Hydroxyphenyl)-3-methylbutane | 60 (0.25) | 1.5157 | 72 | 140 (0.08) | 1.5713 |
| 2-(4-Hydroxyphenyl)-3-methylbutane | 110 (0.8) | m.p. 73° | 109 | 155 (0.1) | 1.5669 |

TABLE IV
Amine salts of dinitrophenols

| | Piperidine (C ₁₀ H ₂₅ N ₃ O ₆), m.p., °C | Morpholine (C ₁₅ H ₂₃ N ₃ O ₆), m.p., °C | Cyclohexylamine (C ₁₇ H ₂₇ N ₃ O ₆), m.p., °C |
|--|---|---|--|
| 2-(2-Hydroxy-3,5-dinitrophenyl)-pentane | 140 | 146 | 189 |
| 2-(4-Hydroxy-3,5-dinitrophenyl)-pentane | 187 | 160 | 169 |
| 3-(2-Hydroxy-3,5-dinitrophenyl)-pentane | 173 | 157 | 192 |
| 3-(4-Hydroxy-3,5-dinitrophenyl)-pentane | 213 | 185 | 217 |
| 2-(2-Hydroxy-3,5-dinitrophenyl)-3-methylbutane | 145 | 153 | 213 (decomp.) |
| 2-(4-Hydroxy-3,5-dinitrophenyl)-3-methylbutane | 199 | 170 | 217 (decomp.) |

Grignard reagent (e.g. 4-methoxypropiophenone and ethyl magnesium bromide), dehydrating the carbinol (6), and hydrogenating the alkene. The 4-alkyl anisoles were demethylated using pyridine hydrobromide and acetic acid but this method failed with the 2-isomers which were accordingly reacted with hydriodic acid and phenol. Nitration of the phenols was done in acetic acid and each dinitrophenol was characterized by the preparation of crystalline salts with morphine, piperidine, and cyclohexylamine.

The dinitrophenols, their derivatives, and intermediates are listed in the tables. All the compounds reported are new except where noted and satisfactory analyses were obtained for all the compounds. These analyses together with experimental details of the preparations are available elsewhere (7, 8).

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SYNTHESIS OF 2- OR 4,6-DINITRO-*sec*-HEXYL PHENOLS

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The synthesis of dinitro-*sec*-pentyl phenols was reported in a recent note (1), and some corresponding *sec*-hexyl homologues are now described and characterized as their crystalline amine salts (2). These compounds are of interest because of the known herbicidal activity of 2,4-dinitro-6-*sec*-butyl phenol (3) and the physiological tests on these compounds will be reported elsewhere.

TABLE I
Properties of alcohols and alkenes

| | Alcohols (C ₁₃ H ₂₀ O ₂) | | Alkenes (C ₁₃ H ₁₈ O) | | Nitrosyl chloride (C ₁₃ H ₁₈ NO ₂ Cl), m.p. °C |
|--|--|-------------------------------------|---|-------------------------------------|--|
| | b.p. °C (0.01 mm) | <i>n</i> _D ²⁵ | b.p. °C (mm) | <i>n</i> _D ²⁵ | |
| 2-(2-Methoxyphenyl)-hexanol-2 | 79 | 1.5095 | 64 (0.04) | 1.5199 | 103 |
| 2-(4-Methoxyphenyl)-hexanol-2 | 68 | 1.5285 | 70 (0.01) | 1.5329 | 86 |
| 3-(2-Methoxyphenyl)-hexanol-3 (6) | 77 | 1.5163 | 80 (0.05) | 1.5204 | 73 |
| 3-(4-Methoxyphenyl)-hexanol-3 (6) | 84 | 1.5204 | 85 (0.4) | 1.5260 | 67 |
| 2-(2-Methoxyphenyl)-3-methylpentanol-3 | 73 | Partial dehydration | 57 (0.04) | 1.5170 | — |
| 2-(4-Methoxyphenyl)-3-methylpentanol-3 | | spontaneous dehydration | 63 (0.04) | 1.5260 | — |
| 2-(2-Methoxyphenyl)-4-methylpentanol-2 | 68 | 1.5260 | 59 (0.01) | 1.5134 | — |
| 2-(2-Methoxyphenyl)-4-methylpentanol-2 | 63 | 1.5128 | 68 (0.04) | 1.5290 | 104 |
| 3-(2-Methoxyphenyl)-2-methylpentanol-3 | 89 | 1.5175 | 70 (0.05) | 1.5228 | — |
| 3-(4-Methoxyphenyl)-2-methylpentanol-3 (8) | 82 | 1.5196 | 84 (0.1) | 1.5240 | — |