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DIMERISATION OF 4-s-BUTENYL PHENOL

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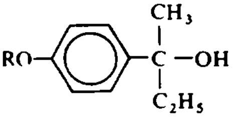
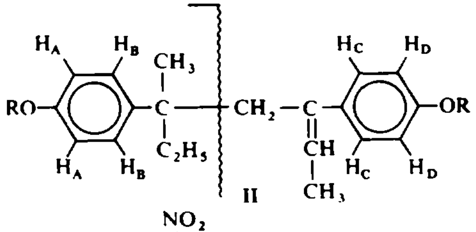
Abstract—The dimeric product obtained by dehydration of ethyl methyl *p*-hydroxyphenyl carbinol using potassium sulphate at 120°, has been shown by NMR and mass spectral data to be 3,5-di-(*p*-hydroxyphenyl)-5-methylhept-2-ene. A similar dehydration of ethyl *p*-methoxyphenyl methyl carbinol yields the monomeric 2-*p*-methoxyphenyl but-2-ene.

THE USE of dinitrophenols as pesticides is well known and some have found successful application as fungicides. The high activity shown by some 4-substituted 2,6- dinitrophenols against apple mildew, caused by *Podosphaera leucotricha* (Ell and Everh.) Salm., has led to extensive synthetic work in this and other laboratories.[1-3] One compound required in this connection was the then unknown 4-s-butyl-2,6-dinitrophenol, which was satisfactorily prepared by reaction of *p*-methoxyacetophenone with ethyl magnesium iodide, followed by dehydration of the resultant carbinol (I; R = Me) and subsequent hydrogenation, demethylation and nitration, the final product having m.p. 47°. If however *p*-hydroxyacetophenone was used, dehydration of the hydroxycarbinol (I; R = H) and a similar series of reactions gave a dinitro phenol m.p. 203° which was obviously anomalous.[4]

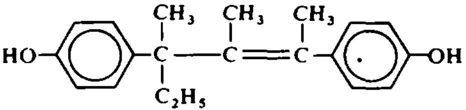
Although methylation of the phenolic carbinol (I; R = H) before dehydration resulted in a final product which was monomeric, it was unlikely that the phenolic OH was involved in a dimerisation process, for two such groups were detected in the dimeric product (II; R = H), and anisic acid was obtained by alkaline potassium permanganate oxidation of the methylated dimer (II; R = Me). The structure II (R = H) assigned to the dimer, is in agreement with and is largely based on spectrographic data. The NMR results given in the Table would appear to exclude the alternative structure (III), possible from dimerisation mechanisms such as suggested by Müller[5] for aryl propenyl compounds.



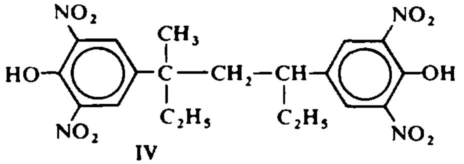
I



II



III



IV

The mass spectra of II (R = H and R = Me) shown in Figs 1 and 2 and the major ion fragmentations support the proposed structure. The predominant reaction in the case of the former (II; R = H) with a molecular ion *m/e* 296, is the formation of the ion *m/e* 149. This probably involves a substituted tropylium ion structure from the fragment shown in II (R = H), and the ion *m/e* 107 most probably represents a hydroxytropylium ion. The only other abundant ion *m/e* 55 appears to arise from C_4 fragments derived from the carbon skeleton between the two aromatic rings.

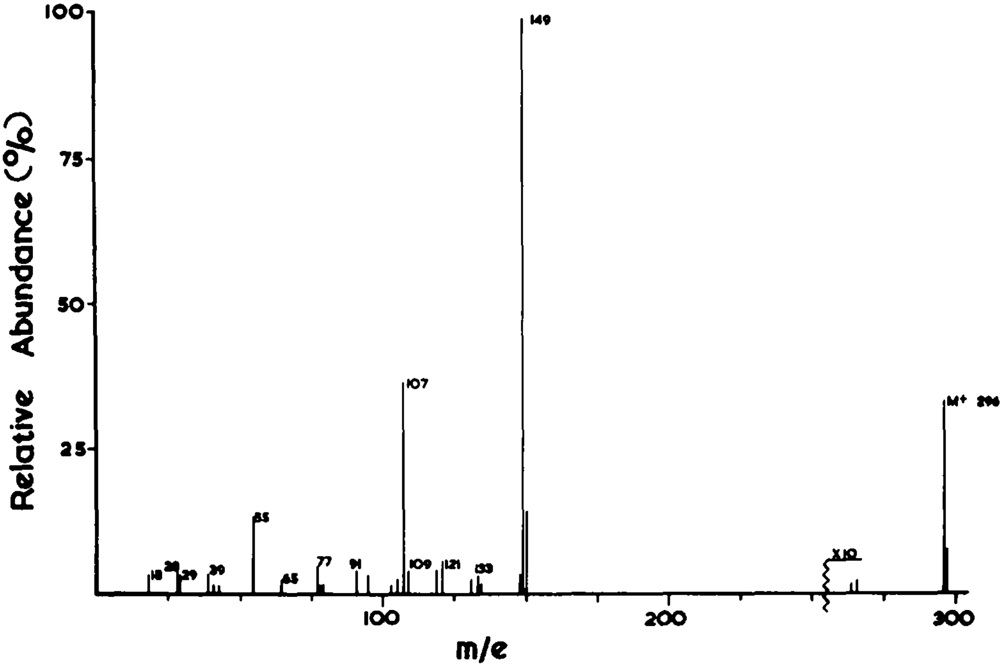


FIG 1. Mass spectrum of 3,5-di-(4-hydroxyphenyl)-5-methylhept-2-ene.

TABLE 1. PMR DATA FOR II (R = H)

τ	Intensity	Multiplicity (*J* in c/s)	Assignment
9·5	3	triplet	CH_3 (of ethyl)
8·9	3	singlet	CH_3
8·55	3	doublet	CH_3 (of ethylidene)
8·4	2	multiplet	CH_2 (of ethyl)
7·3	2	singlet	CH_2
5·2	2	broad singlet	phenolic OH
4·4	1	quadruplet	CH (of ethylidene)
3·4	4	doublet (8)	H_A, H_D
3·1	2	doublet (8)	H_B
3·0	2	doublet (8)	H_C

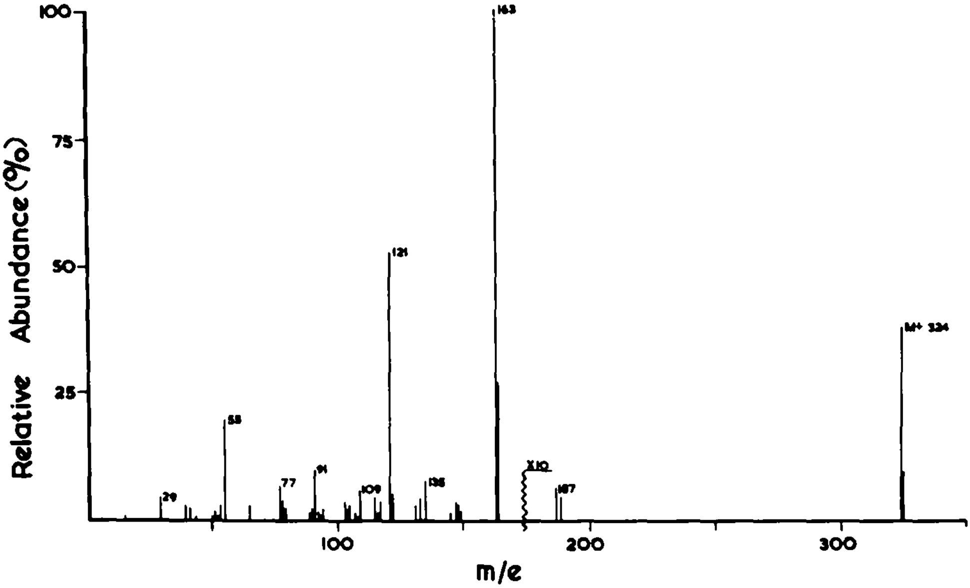


FIG 2. Mass spectrum of 3,5-di-(4-methoxyphenyl)-5-,ethyl-hept-2-ene.

EXPERIMENTAL

IR spectra were determined for liquid films or nujol mulls with a Perkin-Elmer 237 Infracord. The ^1H NMR spectra were obtained using a Varian HA 100 (100 MHz) instrument with $CDCl_3$ as solvent and TMS as internal reference. Mass spectra were measured on an LKB 9000.

Dry solvents refer to molecular sieve-dried materials and light petroleum refers to fraction b.p. 40–60° unless otherwise stated.

TLC was carried out using Merck's Kieselgel G and column chromatography using Kieselgel (0·05–0·2 mm) or alumina (Grade II).

Ethyl p-*hydroxyphenyl methyl carbinol.* *p*-Hydroxyacetophenone (10 g) in dry ether (30 ml) was added dropwise to a stirred soln of the Grignard reagent prepared from Mg (5·2 g) and EtBr (24 g) in dry ether (100 ml). After refluxing the mixture for 1 hr the sticky complex was hydrolysed with NH_4OH aq, and the ether layer washed with water and dried (Na_2SO_4). Removal of the solvent gave a solid (11·5 g) which crystallized from benzene and had m.p. 123°. (Found: C, 72·0; H, 8·7. $C_{10}H_{14}O_2$ requires: C, 72·3; H, 8·4%). Ethyl *p*-methoxyphenyl methyl carbinol was obtained by methylation of this product in alkaline soln by shaking with dimethyl sulphate first in the cold (30 min) and then at 100° (15 min). Isolated by extraction with ether, it was an oil which was purified by elution from a silica column using light petroleum containing 0·5% ether. (Found: C, 73·1; H, 8·8. $C_{11}H_{16}O_2$ requires: C, 73·3; H, 8·9%). It was also prepared by reaction of *p*-anisyl magnesium bromide with ethyl methyl ketone and by reaction of ethyl magnesium bromide with *p*-methoxyacetophenone.

3,5-*Di*-(4-*hydroxyphenyl*)-5-*methylhept*-2-*ene.* The above carbinol (10·2 g) was heated for 30 min at 120° with powdered fused $KHSO_4$ (10 g). The cooled melt was extracted with hot MeOH, filtered and water added gradually until just turbid. After keeping overnight, the product crystallized in needles, m.p. 123–124°, unchanged by recrystallization from benzene–light petroleum (b.p. 80–100°). (Found: C, 80·8; H, 8·1%. Mass spectral base peak M^+ 296. $(C_{10}H_{12}O)_2$ requires: C, 81·1; H, 8·1%. M.W. 296); ν_{max} 1665 cm^{-1} (substituted olefine). Methylation of this product in alkaline soln with dimethyl sulphate gave an oil, insoluble in aqueous 10% NaOHaq, which was purified by elution from a silica column using light petroleum. (Found: C, 81·45; H, 8·8%. M^+ 324. $(C_{11}H_{14}O)_2$ requires: C, 81·5; H, 8·6%. M.W. 324). Oxidation with alkaline $KMnO_4$ gave anisic acid m.p. 182°, undepressed by admixture with an authentic specimen.

3,5-*Di-(4-hydroxyphenyl)-5-methylheptane.* A soln of 3,5-di-(4-hydroxyphenyl)-5-methylhept-2-ene (1 g) in EtOH (5 ml) was shaken with Pd-C (0·1 g) in hydrogen at 22° and 755 mm, until there was no further uptake of gas. The amount absorbed (87·5 ml) is in agreement with the presence of one double bond. Filtration of the soln and removal of the solvent, left an oil, b.p. 258–264°/10 mm which did not decolorize $KMnO_4$ soln. (Found: C, 80·3; H, 8·7. $C_{20}H_{26}O_2$ requires: C, 80·5; H, 8·7%).

3,5-*Di-(4-hydroxy-3,5-dinitrophenyl)-5-methylheptane.* A soln of the above phenol (3·4 g) in AcOH (8 ml) was added dropwise to a stirred mixture of HNO_3 (*d* 1·5, 5·1 ml) and AcOH (9·5 ml) kept below 10°. Stirring was continued after the removal of the ice-bath and the temp rose to 31°. After keeping overnight at laboratory temp, the crystalline product was collected, washed with AcOH and then recrystallized from aqueous AcOH. It had m.p. 204–205°. (Found: C, 50·4; H, 4·6; N, 11·3%. M^+ 478. $C_{20}H_{22}N_4O_{10}$ requires: C, 50·2; H, 4·6; N, 11·7%. M.W. 478). The orange coloured piperidine salt, prepared in acetone soln, crystallized from benzene–light petroleum, and had m.p. 198–199°. (Found: C, 55·6; H, 6·8; N, 13·2. $C_{30}H_{44}N_6O_{10}$ requires: C, 55·6; H, 6·8; N, 13·0%).

p-*s-Butyl phenol.* Ethyl *p*-methoxyphenyl methylcarbinol (3·2 g) was heated with an equal weight of finely powdered fused $KHSO_4$ at 120° for 20 min. The product, which was isolated with ether, was an oil showing two spots (TLC). It was shaken in EtOH (20 ml) with Pd-C (0·3 g) in hydrogen until there was no further uptake of gas, the soln filtered and the solvent distilled off. The residual oil (3·1 g) which showed only a single spot (TLC) was refluxed in AcOH (12 ml) with HI (*d*, 1·7, 15 ml) for 6 hr. The product, isolated by dilution and extraction with ether, had b.p. 110–120°/14 mm and solidified on cooling (2·5 g). Crystallized from light petroleum it had m.p. 61–62°. (Found: C, 79·6; H, 9·6. Calc for $C_{10}H_{14}O$: C, 80·0; H, 9·9%). Dewar and Puttnam[6] give m.p. 58·5–59°.

p-*s-Butyl-2,6-dinitrophenol.* The phenol (1 g) was nitrated as described earlier for the dimeric compound using HNO_3 (*d*, 1·5, 1·5 ml). The product after purification on an alumina column, was a solid which crystallized from light petroleum in yellow plates, m.p. 46·5–47°. (Found: C, 49·8; H, 5·1; N, 11·7. Calc for $C_{10}H_{12}N_2O_5$: C, 50·0; H, 5·0; N, 11·7%). Pianka and Sweet[7] give m.p. 44°. The piperidine salt, prepared in benzene soln crystallized from benzene–light petroleum (b.p. 60–80°) and had m.p. 210°. (Found: C, 55·6; H, 7·2; N, 13·0. $C_{15}H_{23}N_3O_5$ requires: C, 55·4; H, 7·1; N, 13·0%).

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