

Structures and Pesticidal Activities of Derivatives of Dinitro-phenols. Part IV.† Preparation of Certain 2-(α -Branched alkyl)-4,6-dinitro- and 4-(α -Branched alkyl)-2,6-dinitro-phenols

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Twenty-one 2-(α -branched alkyl) phenols and thirty-one 4-(α -branched alkyl) phenols with alkyl groups containing from 5 to 13 carbon atoms were synthesised by condensation, in ether, of a 2- or 4-acyl-phenol or the more soluble -anisole with an alkylmagnesium bromide, dehydration to the alkenyl derivative, hydrogenation, and, where required, demethylation of the anisole. The 2- and 4-alkyl phenols were converted to 2-alkyl-4,6-dinitro- and 4-alkyl-2,6-dinitro-phenols for testing against the causal agents of powdery mildew of apple *Podosphaera leucotricha* (Ell. and Everh.) Salm., of barley *Erysiphe graminis* Mérat, and of cucumber *Erysiphe cichoracearum* Mérat.

FOLLOWING the observation of variations in activities against *Podosphaera leucotricha*, *Erysiphe graminis*, and *Erysiphe cichoracearum* of carbonates of capryldinitrophenol,^{1,2} prepared by nitrating the product of condensation of octan-2-ol with phenol in the presence of an acid, we decided to synthesise and investigate the

activity against these organisms of several 2-(α -branched alkyl)-4,6-dinitro- and 4-(α -branched alkyl)-2,6-dinitro-phenols.

The literature abounds in papers and patents dealing with the alkylation of phenols. Thus phenol has been treated with various aliphatic alcohols or alkenes in

† Part III, M. Pianka and J. D. Edwards, *J. Sci. Food Agric.*, 1967, **18**, 355.

¹ M. Pianka and D. J. Polton, B.P. 1,019,451/1966.

² M. Pianka, *Chem. and Ind.*, 1967, in the press.

the presence of sulphuric acid,³ aluminium chloride,⁴ hydrochloric acid and zinc chloride,^{5,6} or of an acid catalyst such as anhydrous hydrogen fluoride or dihydroxyfluoroboric acid.⁷ Huston *et al.*^{8,9} condensed various s-aliphatic alcohols with benzene or phenol in the presence of aluminium chloride and obtained mixtures of alkyl benzenes or alkyl phenols. The formation of mixtures of isomers in this type of condensation had been observed also by others.^{4,10} Huston and Kaye⁸ suggested that the mixtures might be formed by the dehydration of the s-alcohol and the addition on to

formation at C-2 to C-6 of the acid-dehydrated octan-2-ol.¹³

For the preparation of our alkyl phenols we decided to follow the general method of Smith *et al.*¹⁴ It involved the Fries rearrangement of the appropriate phenyl ester, separation of the resulting 2- and 4-acyl phenols, methylation as required to improve solubility in ether, condensation with the appropriate alkylmagnesium bromide, decomposition of the alcohol, dehydration, distillation of the alkenyl compound, hydrogenation over 10% palladised charcoal, and demethylation, where

TABLE I
Details of preparation of 2-alkenyl anisoles $R^1CH:CR^2 \cdot C_6H_4 \cdot OMe$ from 2-acyl anisole $R^3CH_2CO \cdot C_6H_4 \cdot OMe$ and Grignard reagent R^4MgBr

No. of compound	R^1	R^2	Grignard reaction				Dehydration reaction		
			R^3	2-Acy anisole moles (ml. of ether)	R^4	Grignard reagent moles (ml. of ether)	Addition time; total reaction time at room temp., hr.	Catalyst	Reaction time at room temp., hr.
1	Pr^a	Me	H	0.27 (40)	Bu^a	0.305 (80)	0.75; 4.5	SA ^b (0.2 ml.)	18
2	Et	Et	Me	0.15 (38)	Pr^a	0.165 (49)	0.3; 2.5	TSA ^d (0.2 g.)	2
3	Bu^a	Me	H	0.27 (40)	Pentyl	0.305 (80)	1.5; 18.5 ^e	SA (0.2 ml.)	6 ^c
4	Pr^a	Et	Me	0.15 (25)	Bu^a	0.165 (50)	1; 18	TSA (0.2 g.)	3.5 ^c
6	Bu^a	Et §	Me	0.314 (50)	Pentyl	0.358 (110)	1.5; 3 ^e	SA (0.25 ml.)	6 ^c
7	Pr^a	Pr^a	Et	0.208 (30)	Bu^a	0.235 (125)	2; 4.5 ^f	SA (0.2 ml.)	4.5 ^c
8	Hexyl	Me	H	0.15 (25)	Heptyl	0.165 (50)	0.2; 18	TSA (0.4 g.)	5 ^g

Yields, physical data, and analyses

No. of compound	Yield* (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
				C	H		C	H
1	72	127.5—132°/17 †	1.5228	81.3	9.45	$C_{13}H_{18}O$	82.1	9.45
2	83	89—90/0.2 ‡	1.5240	81.15	9.1	$C_{13}H_{18}O$		
3	84	144—147/18	1.5165	82.65	9.95	$C_{14}H_{20}O$	82.35	9.8
4	82	128—130/10	1.5187	82.35	10.9	$C_{14}H_{20}O$		
6	64	138—142/12	1.5120	82.65	9.95	$C_{15}H_{22}O$	82.55	10.1
7	38	89—96/1	1.5140	82.2	9.8	$C_{15}H_{22}O$		
8	59	116—119/0.6	1.5120	83.05	10.25	$C_{16}H_{24}O$	82.75	10.35

* Yields refer to fractions of wider boiling ranges, mainly up to 5°, used for next steps. † Lit.,²⁷ b. p. 64°/0.04 mm., n_D^{25} 1.5199. ‡ Lit.,²⁷ b. p. 80°/0.05 mm., n_D^{25} 1.5204. § Lit.,¹⁶ no physical data nor analyses.

Symbols used in Tables 1—4: ^a Refluxed for a further hr. ^b Concentrated sulphuric acid. ^c Heated on steam-bath. ^d Toluene-p-sulphonic acid. ^e Refluxed for a further 1.5 hr. ^f Refluxed for a further 2.5 hr. ^g Refluxed in benzene. ^h The acylphenol was added in portions to the ether solution of the Grignard reagent. ⁱ Heated at 160°. ^j Added at 0°. ^k Refluxed with xylene (Dean-Stark). ^l Heated at 50°. ^m Refluxed with benzene (Dean-Stark).

either of the two positions of the resulting olefin. Kirby *et al.*^{11–13} showed that the phenol obtained from the hydrolysis of dinocap (the crotonate of 'capryldinitrophenol' obtained on nitrating the product of condensation of octan-2-ol with phenol in the presence of an acidic agent) (cf. ref. 19) contains 2,6-dinitro-4-(1-methylheptyl)-, (1-ethylhexyl)-, and (1-propylpentyl)-phenols and the corresponding 2,4-dinitro-6-alkylphenols. They ascribed the production of the six isomers to carbonium ion

necessary, with hydrobromic acid and glacial acetic acid. Dutton *et al.*¹⁵ employed pyridinium bromide-acetic acid for the demethylation of the 4-alkyl anisoles and hydriodic acid-phenol for the demethylation of the 2-alkyl anisoles. Byrde *et al.*¹⁶ used hydriodic acid and a 30 hr. period of reflux. The method we used gave smooth demethylation in good yields.

¹⁰ V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, 1940, **5**, 253.

¹¹ A. H. M. Kirby, *Meded. Landb Hoogeschool Opzoek Stns Gent*, 1964, **29**, 976.

¹² A. H. M. Kirby and L. D. Hunter, *Nature*, 1965, **208**, 189.

¹³ A. H. M. Kirby, E. L. Frick, and M. Gratwick, *Ann. Appl. Biol.*, 1966, **57**, 211.

¹⁴ L. I. Smith, H. E. Ungnade, W. M. Lauer, and R. M. Leekley, *J. Amer. Chem. Soc.*, 1939, **61**, 3079.

¹⁵ G. G. S. Dutton, M. E. D. Hillman, and J. G. Moffatt, *Canad. J. Chem.*, 1964, **42**, 480.

¹⁶ R. J. W. Byrde, D. R. Clifford, and D. Woodcock, *Ann. Appl. Biol.*, 1966, **57**, 223.

³ H. E. Buc, U.S.P. 2,104,412/1938.

⁴ I. P. Tsukervanik and Z. N. Nazarova, *J. Gen. Chem. (U.S.S.R.)*, 1937, **7**, 623.

⁵ R. R. Read, U.S.P. 2,242,325/1941.

⁶ R. R. Read, U.S.P. 2,391,798/1945.

⁷ L. Spiegler and J. M. Tinker, *J. Amer. Chem. Soc.*, 1939, **61**, 1002.

⁸ R. C. Huston and I. A. Kaye, *J. Amer. Chem. Soc.*, 1942, **64**, 1576.

⁹ R. C. Huston, R. L. Guile, D. L. Bailey, R. J. Curtis, and M. T. Esterdahl, *J. Amer. Chem. Soc.*, 1945, **67**, 899.

Dehydration of the alcohol resulting from the reaction of an acyl-phenol or -anisole and an alkylmagnesium bromide could give rise to a mixture of alkenyl isomers. For the next step involving hydrogenation fractions of

The i.r. spectra of 4-(1-methylhexyl)-, 4-(1-methylheptyl)-, 4-(1-ethylhexyl)-, 4-(1-propylpentyl)-, 4-(1-methyloctyl)-, 4-(1-ethylheptyl)-, 4-(1-methylnonyl)-, 4-(1-ethylnonyl)-, and 4-(1-butylheptyl)-phenol in carbon

TABLE 2
Details of preparation of 4-alkenyl anisoles $R^1CH:CR^2 \cdot C_6H_4 \cdot OMe$ from 4-acyl anisole $R^3CH_2CO \cdot C_6H_4 \cdot OMe$ and Grignard reagent R^4MgBr

No. of compound	R^1	R^2	Grignard reaction				Dehydration reaction		
			4-Acyl anisole moles (ml. of ether)	R^3	Grignard reagent moles (ml. of ether)	R^4	Addition time; total reaction time at room temp., hr.	Catalyst	Reaction time at room temp., hr.
17	Me	Et	Me	0.15 (75)	Et	0.165 (150)	1.2; 3.75	TSA (0.5 g.)	24
18	Et	Et	Me	0.274 (50)	Pr ^a	0.371 (100)	0.75; 6.25	SA (0.25 ml.)	19 ^c
19	Bu ^a	Me	H	0.3 ^b	Pentyl	0.36 (200)	6	KHSO ₄ (50 g.)	1 ^f
20	Pr ^a	Et	Me	0.133 (50)	Bu ^a	0.133 (75)	0.5; 3	no catalyst	8.5 ^k
21	Et	Pr ^a	Et	0.252 (40)	Pr ^a	0.341 (150)	0.5; 3	SA (0.25 ml.)	16 ^l
23	Bu ^a	Et [§]	Me	0.153 (5)	Pentyl	0.173 (52)	0.3; 3	SA (5 ml.)	16 ^f
25	Hexyl	Me	H	0.2 (50)	Heptyl	0.22 (65)	0.3; 2	TSA (0.2 g.)	2 ^c
26	Pentyl	Et	Me	0.124 (25)	Hexyl	0.391 (150)	0.3; 3	KHSO ₄ (32 g.)	1 ^f
28	Pr ^a	Bu ^a	Pr ^a	0.097 (20)	Bu ^a	0.12 (40)	72	TSA (0.2 g.)	3 ^c
29	Heptyl	Me	H	0.1 (25)	Octyl	0.11 (40)	0.2; 17	TSA (0.3 g.)	0.3 ^c
30	Hexyl	Et	Me	0.2 (50)	Heptyl	0.22 (65)	18	TSA (0.2 g.)	2 ^c
31	Pentyl	Pr ^a	Et	0.15 (30)	Hexyl	0.165 (50)	1 ^a	TSA (0.2 g.)	2.75 ^c
33	Octyl	Me	H	0.1 (25)	Nonyl	0.11 (40)	0.1; 2.5	TSA (0.3 g.)	18
34	Heptyl	Et	Me	0.15 (75)	Octyl	0.157 (75)	0.1; 17.5	TSA (0.5 g.)	0.2; ^c 72
35	Hexyl	Pr ^a	Et	0.15 (75)	Heptyl	0.165 (75)	0.2; 18	TSA (0.5 g.)	0.3; 72
36	Pentyl	Bu ^a	Pentyl	0.1 (20)	Bu ^a	0.11 (40)	3 ^f	TSA (0.2 g.)	2.5 ^c
37	Bu ^a	Pentyl	Bu ^a	0.2 (50)	Pentyl	0.22 (65)	1; 20	TSA (0.2 g.)	3.5 ^c
38	Octyl	Et	Me	0.1 (25)	Nonyl	0.11 (40)	0.2; 17	TSA (0.3 g.)	0.3; ^c 16
39	Heptyl	Pr ^a	Et	0.1 (25)	Octyl	0.165 (50)	0.3; 2.75	TSA (0.5 g.)	5
41	Pentyl	Pentyl	Bu ^a	0.105 (25)	Hexyl	0.115 (40)	0.3; 4.3	TSA (0.2 g.)	2 ^c
42	Octyl	Pr ^a	Et	0.088 (25)	Nonyl	0.11 (40)	0.2; 18 ^a	TSA (0.3 g.)	18
44	Pentyl	Hexyl	Pentyl	0.1 (25)	Hexyl	0.11 (40)	0.3; 3	TSA (0.2 g.)	2 ^c

Yields, physical data, and analyses

No. of compound	Yield* (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
				C	H		C	H
17	83	135—137°/20 †	1.5317	82.25	9.3	C ₁₂ H ₁₆ O	81.8	9.1
18	79	137—142/15 ‡	1.5277	81.5	9.5	C ₁₃ H ₁₈ O	82.1	9.45
19	52	145—148/11—12	1.5278	82.3	9.9	C ₁₄ H ₂₀ O	82.35	9.8
20	45	142—148/11—12	1.5275	81.75	9.5	C ₁₄ H ₂₀ O		
21	69	145—150/17—18	1.5239	82.1	9.85	C ₁₄ H ₂₀ O		
23	81	160—166/16	1.5252	82.1	9.75	C ₁₅ H ₂₂ O	82.55	10.1
25	77	147.5—149/2.1	1.5208	82.0	10.45	C ₁₅ H ₂₄ O	82.75	10.35
26	82	170—173/16	—	82.85	10.6	C ₁₆ H ₂₄ O		
28	83	173—178/19	1.5183	83.2	10.4	C ₁₆ H ₂₄ O		
29	47	172.5/5	1.5198	82.55	10.45	C ₁₇ H ₂₆ O	82.9	10.55
30	82	151.5—152/2	1.5161	83.2	10.7	C ₁₇ H ₂₆ O		
31	74	127—128/0.65	1.5155	82.45	10.7	C ₁₇ H ₂₆ O		
33	68	159/1.7	1.5081	82.1	10.6	C ₁₈ H ₂₈ O	83.1	10.75
34	68	133/0.4	1.5124	83.2	10.5	C ₁₈ H ₂₈ O		
35	81	128/0.5	1.5104	82.95	10.5	C ₁₈ H ₂₈ O		
36	80	125.5—127/0.45	1.5186	83.7	10.75	C ₁₈ H ₂₈ O		
37	92	156.5—166/0.4	1.5150	83.0	9.9	C ₁₈ H ₂₈ O		
38	73	183/5.9	1.5101	82.4	10.5	C ₁₉ H ₃₀ O	83.2	10.95
39	62	151—160/1.2	1.5094	83.0	10.95	C ₁₉ H ₃₀ O		
41	76	131—133/0.4	1.5095	84.15	11.1	C ₁₉ H ₃₀ O		
42	90	170/2.7	1.5081	82.85	11.05	C ₂₀ H ₃₂ O	83.35	11.1
44	83	140—142/0.4	1.5090	83.0	11.25	C ₂₀ H ₃₂ O		

* Yield refers to fractions of wider boiling ranges, mainly up to 5°, used for the next steps. † Lit.,¹⁵ b. p. 58°/0.03 mm. n_D^{25} 1.5310. ‡ Lit.,²⁷ b. p. 85°/0.4 mm., n_D^{25} 1.5260. § Lit.,¹⁶ no physical data nor analyses.

boiling ranges of about 5° were used and the yields in Tables 1—4 are calculated on this basis. For analyses and observation of their physical characteristics the alkenyl compounds were redistilled. We assume, with Woodcock and his co-workers,^{16,17} that the fractions have the structures reported in Tables 1—4.

disulphide solution showed absorption bands at 828 cm^{-1} confirming *para*-disubstitution; 2-(1-methylheptyl)- and 2-(1-propylpentyl)-phenol showed bands at 750—748 cm^{-1} confirming *ortho*-disubstitution. The phenols also showed hydroxy-bands at 3620—3610

¹⁷ M. Clarke and D. Woodcock, *J. Chem. Soc.*, 1962, 519.

TABLE 3
Details of preparation of 2-alkenyl phenols $R^1CH:CR^2 \cdot C_6H_4 \cdot OH$ from 2-acyl phenol $R^3CH_2 \cdot CO \cdot C_6H_4 \cdot OH$ and Grignard reagent R^4MgBr

No. of compound	R^1	R^2	Grignard reaction				Dehydration reaction	
			R^3	2-Acyl phenol moles (ml. of ether)	Grignard reagent moles (R^4 (ml. of ether))	Addition time; total reaction time at room temp., hr.	Catalyst	Reaction time at room temp., hr.
5	Pentyl	Me	H	0.15 (75)	Hexyl 0.45 (150)	1; 4	TSA (0.5 g.)	6 ^e
6 †	Bu ^a	Et	Me	0.2 (82)	Pentyl 0.593 (180)	2; 4-25 ^e	KHSO ₄ (40 g.)	1
7 †	Pr ^a	Pr ^a	Et	0.54 (200)	Butyl 1.61 (400)	1; 96	TSA (0.5 g.)	4-75 ^m
9	Bu ^a	Pr ^a	Et	0.6 (300)	Pentyl 1.8 (600)	72	TSA (0.5 g.)	6-5 ⁿ
10	Pr ^a	Bu ^a	Pr ^a	0.15 (75)	Butyl 0.45 (150)	16	TSA (0.5 g.)	24
11	Hexyl	Et	Me	0.15 (75)	Heptyl 0.45 (150)	18	TSA (0.5 g.)	2-3 ^e
12	Pentyl	Pr ^a	Et	0.15 (50)	Hexyl 0.45 (150)	0.5; 2.5	TSA (0.5 g.)	16
13	Bu ^a	Bu ^a	Bu ^a	0.15 (75)	Bu ^a 0.45 (150)	0.7; 48	TSA (0.5 g.)	2
14	Bu ^a	Pentyl	Bu ^a	0.15 (50)	Pentyl 0.45 (150)	2	TSA (0.5 g.)	24
15	Pentyl	Pentyl	Bu ^a	0.15 (75)	Hexyl 0.45 (150)	2	TSA (0.5 g.)	3 ^e
16	Pentyl	Hexyl	Pentyl	0.15 (50)	Hexyl 0.45 (125)	0.5; 18	TSA (0.3 g.)	0.2; ^e 16

Yields, physical data, and analyses

No. of compound	Yield* (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
				C	H		C	H
5	42	139—144°/12—13	1.5140	81.95	9.55	C ₁₄ H ₂₀ O	82.35	9.8
6	41	136—139/14	1.5148	82.05	9.75	C ₁₄ H ₂₀ O		
7	53	140—146/17 †	1.5161					
9	43	104—112/0.7	—	82.2	10.0	C ₁₅ H ₂₂ O	82.55	10.1
10	30	86/0.3	1.5120	82.9	10.45	C ₁₅ H ₂₂ O		
11	40	107/0.45	1.5081	82.9	10.2	C ₁₆ H ₂₄ O	82.75	10.35
12	39	99—100/0.4	1.5080	82.15	10.4	C ₁₆ H ₂₄ O		
13	28	99/0.45	1.5100	82.9	9.95	C ₁₆ H ₂₄ O		
14	38	109.5—110/0.45	1.5060	83.5	10.6	C ₁₆ H ₂₄ O	82.9	10.55
15	41	123/0.55	1.5020	82.55	10.35	C ₁₇ H ₂₆ O	83.1	10.75
16	48	147/1.1	1.5031	82.7	11.0	C ₁₉ H ₃₀ O	83.2	10.95

* Yield refers to fractions of wider boiling ranges, mainly up to 5°, used for the next steps. † Prepared also as the anisole. ‡ Lit.,¹⁷ b. p. 136—144°/17 mm., n_D^{14} 1.513. § Lit.,¹⁷ b. p. 130—140°/15 mm., n_D^{15} 1.522.

TABLE 4
Details of preparation of 4-alkenyl phenols $R^1CH:CR^2 \cdot C_6H_4 \cdot OH$ from 4-acyl phenol $R^3CH_2 \cdot CO \cdot C_6H_4 \cdot OH$ and Grignard reagent R^4MgBr

No. of compound	R^1	R^2	Grignard reaction				Dehydration reaction	
			R^3	4-Acyl phenol moles (ml. of ether)	Grignard reagent moles (R^4 (ml. of ether))	Addition time; total reaction time at room temp., hr.	Catalyst	Reaction time at room temp., hr.
22	Pentyl	Me †	H	0.2 ^A	Hexyl 0.593 (80)	9.5	KHSO ₄ (40 g.)	1.5 ⁱ
24	Pr ^a	Pr ^a †	Et	0.2 (170)	Bu ^a 0.59 (200)	0.3; 6	KHSO ₄ (47 g.)	1 ⁱ
27	Bu ^a	Pr ^a	Et	0.12 (40)	Pentyl 0.36 (120)	0.1; 17	TSA (0.5 g.)	0.1; ^e 72
28 †	Pr ^a	Bu ^a	Pr ^a	0.1 (50)	Bu ^a 0.3 (90)	0.2; 17.5	TSA (0.3 g.)	0.2 ^e
32	Bu ^a	Bu ^a	Pr ^a	0.1 (35)	Pentyl 0.3 (100)	0.1; 17	TSA (0.3 g.)	0.2; ^e 72
35 †	Hexyl	Pr ^a	Et	0.075 (50)	Heptyl 0.25 (60)	1; 16	TSA (0.3 g.)	0.2; ^e 16
40	Hexyl	Bu ^a	Pr ^a	0.15 (50)	Heptyl 0.45 (150)	0.6; 18	TSA (0.5 g.)	0.3; ^e 72
42	Heptyl	Bu ^a	Pr ^a	0.1 (30)	Octyl 0.25 (80)	0.3; 2.5	TSA (0.5 g.)	0.25 ^e
43	Hexyl	Pentyl	Bu ^a	0.15 (75)	Heptyl 0.45 (150)	1.5	TSA (0.75 g.)	2 ^e

Yields, physical data, and analyses

No. of compound	Yield* (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
				C	H		C	H
22	22	164—167°/12	1.5097	81.35	10.7	C ₁₄ H ₂₀ O	82.35	9.8
24	59	159—160/12	1.5250	82.15	9.8	C ₁₄ H ₂₀ O		
27	76	135—140/1.5	1.5200	81.6	10.05	C ₁₅ H ₂₂ O	82.55	10.1
28 †	90	152—154.5/5	1.5230	83.3	10.4	C ₁₅ H ₂₂ O		
32	90	152—156/2.5		82.3	10.5	C ₁₆ H ₂₄ O	82.75	10.35
35 †	71	152/1	1.5196	83.15	10.95	C ₁₆ H ₂₄ O	82.9	10.55
40	91	148.5/0.7	1.5171	82.6	10.45	C ₁₆ H ₂₄ O	83.1	10.75
42	83	159—164/0.95	1.5170	82.4	10.4	C ₁₇ H ₂₆ O	83.2	10.95
43	53	150/0.4	1.5079	82.5	11.0	C ₁₉ H ₃₀ O		

* Yield refers to fractions of wider boiling ranges, mainly up to 5°, used for the next steps. † Lit.,¹⁸ no physical data nor analyses. ‡ Prepared as the anisole.

Org.

cm.⁻¹. ¹H N.m.r. measurements of the above 4-alkyl phenols in deuteriochloroform solution showed two doublets ($J = 9$ c./sec.) centred at τ 2.93—2.98 and 3.24—3.26 (τ 3.02—3.07 and 3.30—3.34 in carbon tetrachloride) for the 3- and 2-protons, respectively; in the 2-alkyl phenols the four adjacent protons were coupled together to give a complex pattern. The ¹H n.m.r. spectra also showed the expected peaks for alkyl groups; sharp peaks at τ 4.80—5.35 in deuteriochloroform (τ 4.17—4.77 in carbon tetrachloride) indicated a largely unbonded hydroxy-group.

Clarke *et al.*¹⁸ nitrated technical grade caprylphenol using 93% sulphuric acid and aqueous 40% sodium nitrate. Other workers^{12,15,17} carried out the nitration in glacial acetic acid. Hester *et al.*¹⁹ nitrated caprylphenol with 70% nitric acid, in ethylene dichloride, at 25—35°. In order to ensure dinitration we heated the alkyl phenols with 35% nitric acid in carbon tetrachloride or ethylene dichloride under reflux. The alkyldinitro-phenols were converted to their mono- or dicyclohexylammonium salts which were recrystallised and from which the pure alkyldinitro-phenols were liberated by acidification. The biological results with these phenols and their esters will be reported elsewhere.

EXPERIMENTAL

2- and 4-Acyl Phenols.—2- and 4-Acetyl-, 2-propionyl-, and 2- and 4-butyryl-phenols were obtained commercially. The following acyl phenols were synthesised by the method of Miller and Hartung:²⁰ 2-valerylphenol, b. p. 138—141°/15 mm., n_D^{20} 1.5337 (lit.,²¹ b. p. 74°/0.1 mm., n_D^{25} 1.5310); 2-hexanoylphenol, b. p. 106—107°/1.2 mm., n_D^{20} 1.5273 (lit.,²¹ b. p. 83°/0.1 mm., n_D^{25} 1.5262); 2-heptanoylphenol, b. p. 104—106°/0.4 mm., n_D^{25} 1.5205 (lit.,²¹ b. p. 94°/0.1 mm., n_D^{25} 1.5211); 4-valerylphenol, b. p. 213°/16 mm., m. p. 63—64° (lit.,²¹ b. p. 160°/1 mm., m. p. 62°); 4-hexanoylphenol, b. p. 220—230°/15 mm., m. p. 59—60° (lit.,²¹ b. p. 167°/1 mm., m. p. 60°); 4-heptanoylphenol, b. p. 166°/0.4 mm., m. p. 88° (from carbon tetrachloride-light petroleum) (lit.,²¹ b. p. 171°/1 mm., m. p. 90°).

2- and 4-Acyl Anisoles.—2- and 4-Acetyl-, 4-propionyl-, and 4-butyryl-anisoles were obtained commercially. The other anisoles were prepared by heating under reflux for 4 hr. the appropriate acyl phenol, 10% molar excess of dimethyl sulphate, and aqueous sodium hydroxide. The cooled reaction mixture was extracted with ether and the unreacted acyl phenol was removed from the ether extract with 25% aqueous sodium hydroxide. The ether layer was washed, dried (Na₂SO₄), and distilled to give: 2-propionylanisole, b. p. 135.5°/16 mm., n_D^{20} 1.5328 (lit.,²² b. p. 125—127°/14 mm.); 2-butyrylanisole, b. p. 83°/0.8 mm., n_D^{20} 1.5340 (lit.,²³ b. p. 146°/17 mm.); 4-valerylanisole, b. p. 175—178°/19 mm., n_D^{20} 1.5330 (lit.,²⁴ b. p. 162°/12 mm.); 4-hexanoylanisole, b. p. 183°/15 mm., 113—114°/0.4 mm., m. p. 34° (lit.,²⁴ b. p. 165°/10 mm., m. p. 38°); 4-heptanoyl-

anisole, b. p. 120—121°/0.4 mm., m. p. 39—40° (lit.,²⁵ b. p. 240°/50 mm., n_D^{25} 1.5114).

Preparation of 2- and 4-Alkenyl-anisoles and -phenols.—
(a) *Grignard reaction.* The 2- or 4-acyl-phenol or -anisole, neat or dissolved in sodium-dried ether, was added with stirring to a solution of the appropriate alkylmagnesium bromide in sodium-dried ether at such a rate as to maintain vigorous reflux. The reaction mixture was allowed to stand at room temperature (and sometimes heated under reflux), poured on to crushed ice, and acidified with dilute sulphuric acid. The ether layer was separated, washed with water, and the ether was distilled off on the steam-bath at 20 mm.

(b) *Dehydration reaction.* To the hot residue was added concentrated sulphuric acid or toluene-*p*-sulphonic acid and the solution was allowed to stand at room temperature or heated; sometimes the residue was dissolved in benzene or xylene and heated under reflux with or without a Dean-Stark trap. The reaction mixture was extracted with light petroleum (b. p. 60—80°) or ether, washed with a dilute aqueous solution of sodium carbonate, then with water, dried (Na₂SO₄), and distilled. If the extracts were not washed some decomposition occurred during distillation. Tables 1—4 summarise the preparation and physical properties of the compounds.

The following alkenyl-anisoles and -phenols were prepared similarly from the appropriate acyl-anisoles or -phenols and alkylmagnesium bromides followed by dehydration with toluene-*p*-sulphonic acid; they were hydrogenated directly and not redistilled for analyses: 2-(1-ethylprop-1-enyl)anisole (b. p. 120—124°/15 mm., n_D^{20} 1.5285), 2-(1-ethylhept-1-enyl)anisole (b. p. 100—110°/0.9 mm., n_D^{20} 1.5084), 4-(1-methylbut-1-enyl)anisole (b. p. 73—75°/0.5 mm., n_D^{20} 1.5408), 4-(1-methylpent-1-enyl)anisole (b. p. 80—85°/0.3 mm., n_D^{20} 1.5350), 2-(1-propylbut-1-enyl)phenol (b. p. 106—118°/2.5 mm., n_D^{20} 1.5219), 2-(1-propyloct-1-enyl)phenol (b. p. 115—122°/0.8 mm., n_D^{20} 1.4981), and 2-(1-butylhept-1-enyl)phenol (b. p. 112—121°/0.8—0.9 mm., n_D^{20} 1.5039).

Attempted Preparation of 2-(1-Propylhex-1-enyl)-, 2-(1-Butylhex-1-enyl)-, and 2-(1-Pentylhex-1-enyl)-anisoles.—Propyl-, butyl-, or pentyl-magnesium bromide was condensed with 2-hexanoylanisole. The alcohols were dehydrated by heating with toluene-*p*-sulphonic acid and the resulting oils distilled. No satisfactory analyses were obtained for the supposed alkenyl anisoles. For the preparation of 2-alkyl phenols with an alkyl group containing more than 9 carbon atoms, 2-alkenyl phenols (from 2-acyl phenol and alkylmagnesium bromide) were used instead of 2-alkenyl anisoles. However, 4-alkenyl anisoles with alkenyl groups containing 10 to 13 carbon atoms were successfully prepared from 4-acyl anisoles and alkylmagnesium bromides.

Preparation of 2- and 4-Alkyl-anisoles and -phenols by Hydrogenation of Alkenyl-anisoles and -phenols.—2- or 4-Alkenyl-phenols or -anisoles were hydrogenated over 10% palladised charcoal, in ethanol, at 2—3 lb./in.² pressure until no more hydrogen was taken up. The solutions were

¹⁸ D. G. Clarke, C. H. McKeever, and E. L. Wolffe, U.S.P. 2,810,767/1957.

¹⁹ W. F. Hester, D. Hill, and W. E. Craig, U.S.P. 2,526,660/1950.

²⁰ E. Miller and W. H. Hartung, *Org. Synth.*, 1943, Coll. Vol. II, p. 543.

²¹ G. G. S. Dutton, T. I. Briggs, B. R. Brown, and R. K. Powell, *Canad. J. Chem.*, 1953, **31**, 837.

²² A. Robertson, W. F. Sandrock, and C. B. Hendry, *J. Chem. Soc.*, 1931, 2426.

²³ J. Novak, F. Šorm, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1954, **19**, 1264.

²⁴ K. Nakazawa, S. Matsuura, and K. Kusuda, *J. Pharm. Soc. Japan*, 1954, **74**, 495.

²⁵ K. Paranjpe, N. L. Phalnikar, and K. S. Nargund, *J. Univ. Bombay*, 1943, **11A**, Pt. 5, 104.

TABLE 5

Details of preparation of 2-alkyl anisoles by hydrogenation of 2-alkenyl anisoles using 10% palladised charcoal *

No. of compound	2-Alkyl group	Moles of alkenyl anisole (ml. of ethanol)	Yield (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
						C	H		C	H
45	1-Ethylpropyl	0.15 (50)	79.5	105—107°/15 †	1.5038 †	80.95	9.9	C ₁₂ H ₁₈ O	80.9	10.1
46	1-Methylpentyl	0.193 (50)	90	125—127/17 ‡	1.4998 ‡	81.15	10.75	C ₁₃ H ₂₀ O	81.25	10.4
47	1-Ethylbutyl	0.125 (20)	77	76—78/1.5 §	1.5010 §	80.45	10.05	C ₁₃ H ₂₀ O		
48	1-Methylhexyl	0.227 (50)	—	139—141/17	1.4975	82.15	10.7	C ₁₄ H ₂₂ O	81.55	10.7
49	1-Ethylpentyl	0.121 (50)	90	95—98/2	1.4973	82.2	10.8	C ₁₄ H ₂₂ O		
50	1-Ethylhexyl	0.2 (40)	92	140—145/15	1.4938	82.5	10.75	C ₁₅ H ₂₄ O	81.85	10.9
51	1-Propylpentyl	0.073 (50)	64	73—79/0.5—0.7	1.4991	82.3	11.1	C ₁₅ H ₂₄ O		
52	1-Methyloctyl	0.0819 (40)	94	105—107/0.6	1.4938	81.95	10.95	C ₁₆ H ₂₆ O	82.05	11.1
53	1-Ethylheptyl	0.142 (50)	82	92—94/0.45	1.4946	81.85	11.0	C ₁₆ H ₂₆ O		

* 2 g. of catalyst were used except for compound no. 50 (1 g.). † Lit.,¹⁵ b. p. 50°/0.91 mm., n_D^{25} 1.5010. ‡ Lit.,²⁷ b. p. 59°/0.02 mm., n_D^{25} 1.5045. § Lit.,¹⁴ b. p. 104—105°/9 mm., n_D^{20} 1.4975—1.4976; lit.,²⁷ b. p. 58°/0.05 mm., n_D^{25} 1.5022.

TABLE 6

Details of preparation of 4-alkyl anisoles by hydrogenation of 4-alkenyl anisoles (Table 2) using 10% palladised charcoal *

No. of compound	4-Alkyl group	Moles of alkenyl anisole (ml. of ethanol)	Yield (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
						C	H		C	H
54	1-Methylbutyl	0.104 (30)	74	70—72°/1 †	1.4995 †	80.75	10.25	C ₁₂ H ₁₈ O	80.9	10.1
55	1-Ethylpropyl	0.125 (50)	78	119—121/20 ‡	1.5005 ‡	80.35	10.2	C ₁₂ H ₁₈ O		
56	1-Methylpentyl	0.129 (30)	85	83—85/1 §	1.4971 §	80.65	10.35	C ₁₃ H ₂₀ O	81.25	10.4
57	1-Ethylbutyl	0.2 (50)	100	129—132/15 ¶	1.4976 ¶	81.65	10.4	C ₁₃ H ₂₀ O		
58	1-Ethylpentyl	0.060 (50)	78	87—91/0.8	1.4955	81.95	11.1	C ₁₄ H ₂₂ O	81.55	10.7
59	1-Propylbutyl	0.20 (50)	90	139—143/15	1.4950	81.4	10.6	C ₁₄ H ₂₂ O		
60	1-Ethylhexyl	0.133 (60)	69	109—111/2.2	1.4942	82.0	10.8	C ₁₅ H ₂₄ O	81.85	10.9
61	1-Methyloctyl	0.149 (40)	95	116—118/0.7	1.4904	80.7	10.8	C ₁₆ H ₂₆ O	82.05	11.1
62	1-Ethylheptyl	0.1 (55)	93	160—162/12	1.4915	81.6	11.05	C ₁₆ H ₂₆ O		
63	1-Butylpentyl	0.081 (50)	91	168—169/20	1.4930	81.85	11.45	C ₁₆ H ₂₆ O		
64	1-Methylnonyl	0.0455 (30)	94	138—145/2	1.4889	82.15	11.4	C ₁₇ H ₂₈ O	82.25	11.3
65	1-Ethylloctyl	0.159 (40)	98	117—118/0.55	1.4898	82.65	11.45	C ₁₇ H ₂₈ O		
66	1-Propylheptyl	0.111 (45)	94	114/0.45	1.4905	81.8	11.5	C ₁₇ H ₂₈ O		
67	1-Methyldecyl	0.066 (40)	86	168—174/5	1.4891	82.8	11.85	C ₁₈ H ₃₀ O	82.45	11.45
68	1-Ethylnonyl	0.1 (40)	94	115—118/0.1	1.4919	82.85	11.25	C ₁₈ H ₃₀ O		
69	1-Propylloctyl	0.122 (40)	94	127/0.6	1.4897	82.8	11.5	C ₁₈ H ₃₀ O		
70	1-Butylheptyl	0.080 (50)	78	116—118/0.4	1.4954	82.25	11.35	C ₁₈ H ₃₀ O		
71	1-Pentylhexyl	0.183 (50)	87	187—193/20	1.4920	82.3	11.35	C ₁₈ H ₃₀ O		
72	1-Ethyldecyl	0.071 (35)	100	158—163/2.2—2.6	1.4865	82.95	11.6	C ₁₉ H ₃₂ O	82.6	11.6
73	1-Propylnonyl	0.060 (40)	76	140—141/0.7	1.4885	82.5	11.35	C ₁₉ H ₃₂ O		
74	1-Pentylheptyl	0.080 (40)	95	149—151/1.3	1.4900	82.85	11.75	C ₁₉ H ₃₂ O		
75	1-Propyldecyl	0.079 (45)	87	176—179/1.5	1.4861	82.95	11.7	C ₂₀ H ₃₄ O	82.75	11.7
76	1-Hexylheptyl	0.083 (40)	85	158—160/1.5	1.4898	82.3	11.7	C ₂₀ H ₃₄ O		

* 2 g. of catalyst were used, except for compounds nos. 58, 60, and 62 (1 g.), and 67 (4 g.). † Lit.,¹⁵ b. p. 68°/0.3 mm., n_D^{25} 1.4970. ‡ Lit.,¹⁵ b. p. 56°/0.02 mm., n_D^{25} 1.5030; lit.,²⁶ b. p. 84—86°/0.4 mm. § Lit.,²⁷ b. p. 60°/0.03 mm., n_D^{25} 1.5012. ¶ Lit.,¹⁴ b. p. 125—125.5°/15 mm., n_D^{20} 1.4988; lit.,²⁷ b. p. 85°/0.1 mm., n_D^{25} 1.4968.

TABLE 7

Details of preparation of 2-alkyl phenols by hydrogenation of 2-alkenyl phenols using 10% palladised charcoal *

No. of compound	2-Alkyl group	Moles of alkenyl phenol (ml. of ethanol)	Yield (%)	B. p./mm.	n_D^{20}	Found (%)		Formula	Required (%)	
						C	H		C	H
82	1-Propylbutyl	0.15 (20)	36	145—148°/15	1.5094	80.35	9.95	C ₁₃ H ₂₀ O	81.25	10.4
83	1-Methylheptyl	0.075 (105)	70	151/11.5 ^a	1.5038 ^a	81.4	10.6	C ₁₄ H ₂₂ O	81.55	10.7
84	1-Ethylhexyl ^b	0.081 (70)	78	145/11	1.5057	81.05	10.55	C ₁₄ H ₂₂ O		
85	1-Propylpentyl ^c	0.028 (40)	94	96—98/0.6	1.5059					
88	1-Propylhexyl	0.15 (45)	30	168—170/15	1.5030	80.75	10.65	C ₁₆ H ₂₄ O	81.85	10.9
89	1-Butylpentyl	0.055 (40)	92	99—100/0.45	1.5045	81.4	10.95	C ₁₆ H ₂₄ O		
90	1-Ethylloctyl	0.06 (40)	90	113—114/0.45	1.4987	81.95	10.7	C ₁₆ H ₂₆ O	82.05	11.1
91	1-Propylheptyl	0.054 (40)	44	108/0.4	1.5005	81.75	11.05	C ₁₆ H ₂₆ O		
92	1-Butylhexyl	0.042 (40)	79	110/0.3	1.5020	82.15	11.4	C ₁₆ H ₂₆ O		
93	1-Propylloctyl	0.076 (30)	88	131.5—135/0.8	1.4976	81.95	11.0	C ₁₇ H ₂₈ O	82.25	11.3
94	1-Butylheptyl	0.069 (30)	89	130—131/1	1.4983	82.5	11.3	C ₁₇ H ₂₈ O		
95	1-Pentylhexyl	0.058 (40)	88	116—117/0.45	1.4984	83.2	11.4	C ₁₇ H ₂₈ O		
96	1-Pentylheptyl	0.061 (40)	90	128—130/0.45	1.4962	81.95	11.1	C ₁₈ H ₃₀ O	82.45	11.45
97	1-Hexylheptyl	0.066 (40)	95	147/0.85	1.4972	82.75	12.0	C ₁₉ H ₃₂ O	82.6	11.6

* 2 g. of catalyst were used, except for compounds nos. 84 (1 g.), 83, 84, and 85 (4 g.).

^a Lit.,¹⁷ b. p. 146—150°/15 mm., $n_D^{14.9}$ 1.509. ^b Lit.,^{12,16} no physical data nor analyses. ^c Cf. Table 9.

TABLE 8

Details of preparation of 4-alkyl phenols by hydrogenation of 4-alkenyl phenols using 10% palladised charcoal *

No. of compound	4-Alkyl group	Moles of alkenyl phenol (ml. of ethanol)	Yield (%)	B. p./mm.	n_D^{20}	Found (%)			Required (%)	
						C	H	Formula	C	H
105	1-Methylheptyl ^a	0.044 (40)	64	163—164°/11	1.5019	81.2	10.6	C ₁₄ H ₂₂ O	81.55	10.7
107	1-Propylpentyl ^a	0.118 (40)	74	124—125/1.8 †		81.85	10.95	C ₁₄ H ₂₂ O		
110	1-Propylhexyl	0.118 (40)	83	167/12	1.5028	81.6	10.9	C ₁₅ H ₂₄ O	81.85	10.9
115	1-Butylhexyl	0.079 (70)	72	186—187/11 †	1.5008	82.05	10.9	C ₁₆ H ₂₆ O	82.05	11.1
118	1-Propyloctyl	0.053 (35)	79	144—145/1 †	1.4993	82.4	11.4	C ₁₇ H ₂₈ O	82.25	11.3
123	1-Butyloctyl	0.136 (40)	92	153.5/1	1.4978	82.2	11.4	C ₁₈ H ₃₀ O	82.45	11.45
126	1-Butylmonyl	0.08 (40)	94	146.5/0.3	1.5021	81.0	11.2	C ₁₉ H ₃₂ O	82.6	11.6
127	1-Pentyloctyl	0.057 (40)	90	150.5/0.9	1.4883	83.2	11.8	C ₁₉ H ₃₂ O		

* 2 g. of catalyst were used, except for compounds nos. 105, 107, and 110 (1 g.). † Solidified to white crystals, m. p. 36—37°. ‡ Solidified to white crystals, m. p. 40—41°.

^a Lit.,^{12,16} no physical data nor analyses.

TABLE 9

Details of preparation of 2-alkyl phenols by demethylation of 2-alkyl anisoles

No. of compound	2-Alkyl group	Period of reflux with HBr-acetic acid, hr.	Yield (%)	B. p./mm.	n_D^{20} (m. p.)	Found (%)			Required (%)	
						C	H	Formula	C	H
77	1-Ethylpropyl	16	81	109—111°/10 ^a	60—62° ^a					
78	1-Methylpentyl	15.5	75	139—142/20 ^b	1.5130 ^b	80.7	10.25	C ₁₂ H ₁₈ O	80.9	10.1
79	1-Ethylbutyl	11	56	92—94/1.5 ^c	1.5144 ^c	80.3	10.0	C ₁₂ H ₁₈ O		
80	1-Methylhexyl	14.5	83	151—154/20	1.5090	81.3	10.45	C ₁₃ H ₂₀ O	81.25	10.4
81	1-Ethylpentyl ^d	24	77	103—105/1.3	1.5099	80.7	10.05	C ₁₃ H ₂₀ O		
84	1-Ethylhexyl ^e	16	75	154—156/18	1.5058					
85	1-Propylpentyl	16	60	153—154/17 ^f	1.5058 ^f	81.8	10.75	C ₁₄ H ₂₂ O	81.55	10.7
86	1-Methyloctyl	15	81	161—162/10	1.5028	82.05	10.75	C ₁₅ H ₂₄ O	81.85	10.9
87	1-Ethylheptyl	15	72	106—108/0.7	1.5040	82.1	10.7	C ₁₅ H ₂₄ O		

^a Lit.,¹⁵ b. p. 61°/0.1 mm., m. p. 64°; lit.,²⁶ m. p. 74—76°. ^b Lit.,²⁷ b. p. 60°/0.01 mm., n_D^{25} 1.5160. ^c Lit.,¹⁴ b. p. 109—111°/10 mm., n_D^{20} 1.5099; lit.,²⁷ b. p. 55°/0.01 mm., n_D^{25} 1.5162. ^d Lit.,¹² no physical data nor analyses. ^e Cf. Table 7. ^f Lit.,¹⁷ b. p. 110—114°/1 mm., n_D^{14} 1.512.

TABLE 10

Details of preparation of 4-alkyl phenols by demethylation of 4-alkyl anisoles

No. of compound	4-Alkyl group	Period of reflux with HBr-acetic acid, hr.	Yield (%)	B. p./mm.	n_D^{20} (m. p.)	Found (%)			Required (%)	
						C	H	Formula	C	H
98	1-Methylbutyl	12	68	89—90°/1 ^{a,j}	1.5148	80.25	9.9	C ₁₁ H ₁₆ O	80.5	9.75
99	1-Ethylpropyl	12	65	140—140.5/20 ^{b,j}	(77—78°) ^b	80.25	9.85	C ₁₁ H ₁₆ O		
100	1-Methylpentyl	15	85	99—100/1 ^{c,j}	1.5111	80.25	10.0	C ₁₂ H ₁₈ O	80.9	10.1
101	1-Ethylbutyl	10	81	150—153/2 ^{d,j}	(49—50°)	80.55	10.1	C ₁₂ H ₁₈ O		
102	1-Methylhexyl	7.5	71	157—159/15 ^{e,j}	1.5075					
103	1-Ethylpentyl ^h	11.5	82	154—155/15 ^{f,j}	(30—31°)					
104	1-Propylbutyl	11	93	158—159/19 ^{g,j}	(61—64°)	81.15	10.35	C ₁₃ H ₂₀ O	81.25	10.4
106	1-Ethylhexyl ^h	7	81	153—154/10	1.5060	81.8	10.7	C ₁₄ H ₂₂ O	81.55	10.7
108	1-Methyloctyl	15	85	140—142/1.3	1.5029	82.2	11.25	C ₁₅ H ₂₄ O	81.85	10.9
109	1-Ethylheptyl ^h	14	70	176—178/15	1.5050	81.4	10.75	C ₁₅ H ₂₄ O		
111	1-Butylpentyl	12	85	180/20	(55°)	81.05	10.95	C ₁₅ H ₂₄ O		
112	1-Methylmonyl	15	51	149/1.7	1.4998	81.85	11.05	C ₁₆ H ₂₆ O	82.05	11.1
113	1-Ethylloctyl	15	90	146/1.3	1.5002	82.95	11.35	C ₁₆ H ₂₆ O		
114	1-Propylheptyl	14	56 ^k	117/0.2	1.5011	81.3	10.95	C ₁₆ H ₂₆ O		
116	1-Methyldecyl	15	75	170—171/1.3	1.4989	82.6	11.6	C ₁₇ H ₂₈ O	82.25	11.3
117	1-Ethylmonyl	15	85	134/0.35	1.4996	82.25	11.3	C ₁₇ H ₂₈ O		
118	1-Propyloctyl	15	92	144—145/1	1.4993					
119	1-Butylheptyl	14	83	123/0.2	1.5949	81.35	11.15	C ₁₇ H ₂₈ O		
120	1-Pentylhexyl	15	76	131.5—132/0.45	1.5010	81.85	10.75	C ₁₇ H ₂₈ O		
121	1-Ethyldecyl	15	64	169/2.6	1.4942	82.75	11.9	C ₁₈ H ₃₀ O	82.45	11.45
122	1-Propylmonyl	12.5	65	162/1.6	1.4976	81.8	10.9	C ₁₈ H ₃₀ O		
124	1-Pentylheptyl	24	72	163—164/1.3	1.4981	81.9	11.45	C ₁₈ H ₃₀ O		
125	1-Propyldecyl	15	73	172—174/1.3	1.4910	82.1	11.75	C ₁₉ H ₃₂ O	82.6	11.6
128	1-Hexylheptyl	16	49	166—169/1.3	1.4994	82.9	11.6	C ₁₉ H ₃₂ O		

^a Lit.,⁸ b. p. 101—103°/2 mm.; lit.,¹⁵ b. p. 84°/0.5 mm., n_D^{25} 1.5132. ^b Lit.,⁸ b. p. 108—117°/2 mm., m. p. 75.5°; lit.,¹⁵ b. p. 83°/0.3 mm., m. p. 72°. ^c Lit.,⁸ b. p. 110—112°/2 mm., lit.,²⁷ b. p. 80°/0.05 mm., n_D^{25} 1.5110. ^d Lit.,⁸ b. p. 133°/4 mm.; lit.,¹⁴ b. p. 134—135°/14 mm.; lit.,²⁷ b. p. 90°/0.03 mm., m. p. 49°. ^e Lit.,⁸ b. p. 140°/4 mm. ^f Lit.,⁸ 117°/2 mm. ^g Lit.,⁸ b. p. 121—123°/2 mm. ^h Lit.,¹² no physical data nor analysis. ⁱ Cf. Table 8. ^j Huston and Kaye (ref. 8) reported the boiling point (m. p.) and analysis, but did not report the experimental details. ^k Some unreacted anisole (30%) was recovered during the distillation.

filtered from the catalyst and fractionated. The details of the preparation and physical data are summarised in Tables 5—8.

Preparation of 2- and 4-Alkyl Phenols by Demethylation of Alkyl Anisoles.—The 4- or 2-alkyl anisole (0.1 mole) was heated under reflux with a mixture of aqueous hydrobromic acid (47—48%; 92 g.) and acetic acid (176 ml.), cooled, and extracted with light petroleum, b. p. 60—80°. The

petroleum extract was washed with water, then shaken with a methanolic solution of 25% aqueous sodium hydroxide (1:1). For anisoles with alkyl chains of 10 to 13 carbon atoms the proportion of methanol was higher (up to 3:1) to avoid retention of the sodium phenoxide in the petroleum layer. The alkaline extract was washed with petroleum and acidified with concentrated hydrochloric acid. The phenol was then extracted with light petroleum,

TABLE 11
Details of preparation of 2-alkyl-4,6-dinitro-phenols
Preparation of cyclohexylamine and dicyclohexylamine salts

No. of compound	2-Alkyl group	Solvent used for nitration (period of reflux, hr.)	Solvent used in the formation of salt	M. p. of cyclohexylamine salt	M. p. of dicyclohexylamine salt	Yield of salt (%)
129	1-Ethylpropyl	N (3)	A	188—190° (F) ^a		74.5
130	1-Methylpentyl	N (3)	N	171—172.5 (G) ^b		66.5
131	1-Ethylbutyl	N (3)	E	156.5—158 (F) ^c		61
132	1-Methylhexyl	N (3)	N	158.5—160 (G) ^d		47
133	1-Ethylpentyl	N (3)	A	149—150 (F) ^e		69
134	1-Propylbutyl	N (3)	A	138 (H)		48
		N (3)	A		190—191° (B)	66
135	1-Methylheptyl	C (1.5)	J	154—155 (H) ^h		62
136	1-Ethylhexyl	C (1.5)	J	135—138 (H) ^f		67
		N (3)	A		151—152.5 (H) ^g	72
137	1-Propylpentyl	N (3.5)	N	125—126 (J)		58
138	1-Methyloctyl	M (4.5)	D		163—164 (K)	68
139	1-Ethylheptyl	N (4)	A		154—155 (K)	54
140	1-Propylhexyl	N (3)	A	<i>i</i>	168—169 (F)	56
141	1-Butylpentyl	N (3)	A		171 (F)	64
142	1-Ethylloctyl	N (6)	N		155 (F)	51
143	1-Propylheptyl	N (3)	A	127—129 (F)		46
144	1-Butylhexyl	N (3.5)	A	<i>i</i>	171—171.5 (F)	46
145	1-Propyloctyl	N (3)	A		152—153.5 (K)	67
146	1-Butylheptyl	N (3)	A		158.5—159.5 (K)	72
147	1-Pentylhexyl	N (3)	A	<i>i</i>	165 (F)	49
148	1-Pentylheptyl	N (5)	D		164 (K)	61
149	1-Hexylheptyl	N (3)	A		156—158 (L)	81

Yields, n_D^{20} , and analyses of 2-alkyl-4,6-dinitro-phenols

No. of compound	2-Alkyl group	Yield of dinitro-phenol (%)	n_D^{20}	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
129	1-Ethylpropyl ¹	67 ^j	1.5730	51.55	5.65	11.2	C ₁₁ H ₁₄ N ₂ O ₅	52.0	5.5	11.05
130	1-Methylpentyl	55 ^j	1.5636	53.7	6.3	10.6	C ₁₂ H ₁₆ N ₂ O ₅	53.75	5.95	10.45
131	1-Ethylbutyl ¹	58 ^j	1.5664	53.15	5.8	10.6	C ₁₂ H ₁₆ N ₂ O ₅			
132	1-Methylhexyl ¹	47 ^j	1.5570	54.35	6.35	9.55	C ₁₃ H ₁₈ N ₂ O ₅	55.35	6.4	9.95
133	1-Ethylpentyl ¹	64 ^j	1.5590	55.2	6.45	10.2	C ₁₃ H ₁₈ N ₂ O ₅			
134	1-Propylbutyl	47 ^j (66 ^k)	1.5590	55.9	6.65	9.6	C ₁₃ H ₁₈ N ₂ O ₅			
135	1-Methylheptyl ¹	60 ^j	1.5516			9.55	C ₁₄ H ₂₀ N ₂ O ₅	56.75	6.75	9.45
136	1-Ethylhexyl ¹	61 ^j (71 ^k)	1.5529			9.4	C ₁₄ H ₂₀ N ₂ O ₅			
			(m. p. 30°)							
137	1-Propylpentyl	57 ^j	1.5540	56.7	6.7	9.2	C ₁₄ H ₂₀ N ₂ O ₅			
			(m. p. 33—34°)							
138	1-Methyloctyl	63 ^k	1.5473	58.1	7.2	8.55	C ₁₅ H ₂₂ N ₂ O ₅	58.05	7.1	9.05
139	1-Ethylheptyl	53 ^k	1.5467	58.15	7.2	9.3	C ₁₅ H ₂₂ N ₂ O ₅			
140	1-Propylhexyl	46 ^k	1.5478	58.65	7.3	8.15	C ₁₅ H ₂₂ N ₂ O ₅			
141	1-Butylpentyl	64 ^k	1.5486	58.0	7.3	9.2	C ₁₅ H ₂₂ N ₂ O ₅			
142	1-Ethylloctyl	48 ^k	1.5433	59.1	7.3	8.3	C ₁₆ H ₂₄ N ₂ O ₅	59.25	7.4	8.65
143	1-Propylheptyl	44 ^j	1.5434	59.05	7.35	8.55	C ₁₆ H ₂₄ N ₂ O ₅			
144	1-Butylhexyl	42 ^k	1.5432	59.2	7.6	8.3	C ₁₆ H ₂₄ N ₂ O ₅			
145	1-Propyloctyl	65 ^k	1.5384	60.4	8.1	8.35	C ₁₇ H ₂₆ N ₂ O ₅	60.35	7.7	8.3
146	1-Butylheptyl	69 ^k	1.5397	60.2	8.0	8.5	C ₁₇ H ₂₆ N ₂ O ₅			
147	1-Pentylhexyl	48 ^k	1.5400	60.25	7.9	8.15	C ₁₇ H ₂₆ N ₂ O ₅			
148	1-Pentylheptyl	60 ^k	1.5362	61.1	7.8	8.7	C ₁₈ H ₂₈ N ₂ O ₅	61.4	7.95	7.95
149	1-Hexylheptyl	80 ^k	1.5320	61.35	7.85	7.65	C ₁₈ H ₂₈ N ₂ O ₅	62.25	8.2	7.65

^a Lit.,¹⁵ m. p. 192°. ^b Lit.,²⁷ m. p. 173°. ^c Lit.,²⁷ m. p. 160°. ^d Lit.,²⁸ m. p. 162°. ^e Lit.,¹² m. p. 151°. ^f Lit.,¹² m. p. 138°. ^g Lit.,¹² m. p. 153—154°. ^h Lit.,¹² m. p. 151—153°. ⁱ The cyclohexylamine salt crystallised with difficulty. ^j From cyclohexylamine salt. ^k From dicyclohexylamine salt. ^l The salts have been previously characterised, but not the alkyldinitro-phenols.

Solvents referred to in Tables 11 and 12: A, di-isopropyl ether; B, propan-2-ol; C, ethylene dichloride; D, light petroleum, b. p. 40—60°; E, light petroleum, b. p. 60—80°; F, aqueous propan-2-ol; G, di-isopropyl ether-propan-2-ol; H, not recrystallised; J, toluene; K, ethanol; L, methanol-acetone; M, methylene dichloride; N, carbon tetrachloride.

TABLE 12
Details of preparation of 4-alkyl-2,6-dinitro-phenols
Preparation of cyclohexylamine salts ^a

No. of compound	4-Alkyl group	Solvent used for nitration (period of reflux, hr.)	Solvent used in the formation of salt	M. p. of cyclohexylamine salt	Yield of salt (%)
150	1-Methylbutyl	N (3)	A	169° ^a	58
151	1-Ethylpropyl	N (3)	A	213—214 ^b	69
152	1-Methylpentyl	N (3)	A	136—137.5 ^c	55
153	1-Ethylbutyl	N (3)	A	197—198 ^d	68
154	1-Methylhexyl	N (3)	A	135—136 ^e	56
155	1-Ethylpentyl	N (3)	E	171—172 ^f	65
156	1-Propylbutyl	N (3)	E	197—199	65
157	1-Methylheptyl	C (3)	D	128—132 ^g	42
158	1-Ethylhexyl	C (1.5)	D	162—164 ^h	76
159	1-Propylpentyl	C (1.5)	D	179.5—181 ⁱ	72
160	1-Methyloctyl	N (4)	A	124—125	57
161	1-Ethylheptyl	N (3)	E	169—170 ^j	76
162	1-Propylhexyl	N (3)	A	167—168	58
163	1-Butylpentyl	N (4)	A	184—185	77
164	1-Methylnonyl	N (3)	E	113—115	55
165	1-Ethylloctyl	N (4.5)	A	160—161	71
166	1-Propylheptyl	N (3)	A	157—158.5	60
167	1-Butylhexyl	C (1.5)	A	183	63
168	1-Methyldecyl	N (3.5)	E	109—110	31
169	1-Ethylnonyl	N (3)	A	155—156	73
170	1-Propylloctyl	N (3)	A	144—145	68
171	1-Butylheptyl	N (3)	A	164—165.5	51
172	1-Pentylhexyl	N (5)	A	183—184	68
173	1-Ethyldecyl	N (3)	E	155—157	67
174	1-Propylmonyl	N (3)	A	143—144	54
175	1-Butyloctyl	N (3)	A	139—140.5	74
176	1-Pentylheptyl	N (3)	A	169—170	56
177	1-Propyldecyl	N (3.5)	D	143—144	48
178	1-Butylmonyl	N (4)	A	131—132.5	61
179	1-Pentyloctyl	N (3)	A	144—145	35
180	1-Hexylheptyl	N (3)	D	161.5—163	48

Yields, n_D^{20} , and analyses of 4-alkyl-2,6-dinitro-phenols

No. of compound	4-Alkyl group	Yield of dinitro-phenol (%)	n_D^{20}	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
150	1-Methylbutyl ^l	48	1.5648	52.4	5.7	10.8	C ₁₁ H ₁₄ N ₂ O ₅	52.0	5.5	11.05
151	1-Ethylpropyl ^l	69	1.5698	52.3	5.95	11.2	C ₁₁ H ₁₄ N ₂ O ₅			
152	1-Methylpentyl ^l	52	1.5575	54.45	6.05	10.55	C ₁₃ H ₁₈ N ₂ O ₅	53.75	5.95	10.45
153	1-Ethylbutyl ^l	67	1.5595	53.7	5.9	9.9	C ₁₂ H ₁₆ N ₂ O ₅			
154	1-Methylhexyl ^l	52	1.5511	56.0	7.05	9.7	C ₁₃ H ₁₈ N ₂ O ₅	55.35	6.4	9.95
155	1-Ethylpentyl ^l	65	1.5526	55.9	6.5	9.3	C ₁₃ H ₁₈ N ₂ O ₅			
156	1-Propylbutyl ^l	63	1.5528	55.4	6.6	9.8	C ₁₃ H ₁₈ N ₂ O ₅			
157	1-Methylheptyl ^l	41	1.5451	57.35	6.85	9.2	C ₁₄ H ₂₀ N ₂ O ₅	56.75	6.75	9.45
158	1-Ethylhexyl ^l	73	1.5470			9.8	C ₁₄ H ₂₀ N ₂ O ₅			
159	1-Propylpentyl ^l	69	1.5482			9.25	C ₁₄ H ₂₀ N ₂ O ₅			
160	1-Methyloctyl ^l	54	1.5406	58.1	7.35	8.8	C ₁₅ H ₂₂ N ₂ O ₅	58.05	7.1	9.05
161	1-Ethylheptyl ^l	75	1.5420	58.1	7.35	9.3	C ₁₅ H ₂₂ N ₂ O ₅			
162	1-Propylhexyl ^l	55	1.5424			8.9	C ₁₅ H ₂₂ N ₂ O ₅			
163	1-Butylpentyl ^l	74	1.5435	57.5	7.05	7.8	C ₁₅ H ₂₂ N ₂ O ₅			
164	1-Methylmonyl ^l	49	1.5359	60.1	7.35	8.7	C ₁₆ H ₂₄ N ₂ O ₅	59.25	7.4	8.65
165	1-Ethylloctyl ^l	65	1.5380	60.15	7.55	8.7	C ₁₆ H ₂₄ N ₂ O ₅			
166	1-Propylheptyl ^l	56	1.5380	58.95	7.4	8.6	C ₁₆ H ₂₄ N ₂ O ₅			
167	1-Butylhexyl ^l	62	1.5382			8.95	C ₁₆ H ₂₄ N ₂ O ₅			
168	1-Methyldecyl ^l	30	m. p. 52—53°	60.15	7.75	8.2	C ₁₇ H ₂₆ N ₂ O ₅	60.35	7.7	8.3
169	1-Ethylnonyl ^l	70	1.5252	60.5	7.7	7.95	C ₁₇ H ₂₆ N ₂ O ₅			
170	1-Propylloctyl ^l	63	1.5343	60.8	7.35	7.75	C ₁₇ H ₂₆ N ₂ O ₅			
171	1-Butylheptyl ^l	49	1.5345	60.1	7.6	8.45	C ₁₇ H ₂₆ N ₂ O ₅			
172	1-Pentylhexyl ^l	64	1.5345	60.75	8.35	8.2	C ₁₇ H ₂₆ N ₂ O ₅			
173	1-Ethyldecyl ^l	63	1.5298	61.65	7.85	8.1	C ₁₈ H ₂₈ N ₂ O ₅	61.4	7.95	7.95
174	1-Propylmonyl ^l	49	1.5304	61.2	7.9	7.45	C ₁₈ H ₂₈ N ₂ O ₅			
175	1-Butyloctyl ^l	73	1.5314	61.65	8.15	8.0	C ₁₈ H ₂₈ N ₂ O ₅			
176	1-Pentylheptyl ^l	53	1.5300	62.05	8.1	7.95	C ₁₈ H ₂₈ N ₂ O ₅			
177	1-Propyldecyl ^l	48	1.5277	62.05	8.3	8.05	C ₁₉ H ₃₀ N ₂ O ₅	62.25	8.2	7.65
178	1-Butylmonyl ^l	59	1.5294	62.0	7.8	7.45	C ₁₉ H ₃₀ N ₂ O ₅			
179	1-Pentyloctyl ^l	31	1.5285	62.15	8.05	7.15	C ₁₉ H ₃₀ N ₂ O ₅			
180	1-Hexylheptyl ^l	46	1.5279	62.25	8.2	7.75	C ₁₉ H ₃₀ N ₂ O ₅			

^a Lit.,¹⁵ m. p. 169°. ^b Lit.,¹⁵ m. p. 217°. ^c Lit.,²⁷ m. p. 138°. ^d Lit.,²⁷ m. p. 200°. ^e Lit.,²⁸ m. p. 133°. ^f Lit.,²² m. p. 173—174°. ^g Lit.,¹² m. p. 129—130°. ^h Lit.,¹² m. p. 163—165°. ⁱ Lit.,¹² m. p. 181—183°. ^j Lit.,¹² m. p. 167—168°. ^k All the cyclohexylamine salts listed in Table 12 were recrystallised from aqueous propan-2-ol. ^l The salts have been previously characterised, but not the alkyl dinitro-phenols.

the petroleum extract was washed with water, dried (Na_2SO_4), and fractionated. The preparation and the physical data of the alkyl phenols are summarised in Tables 9 and 10.

Preparation of 2-Alkyl-4,6-dinitro- and 4-Alkyl-2,6-dinitro-phenols.—The alkyl phenol (0.1 mole), in carbon tetrachloride or ethylene dichloride (38 ml.), was heated under reflux with nitric acid (35%, 50 ml.). The organic layer was separated and concentrated on a steam-bath under reduced pressure. The residue was dissolved in a water immiscible solvent, washed with water, dried (Na_2SO_4 and charcoal), and treated with a slight excess of mono- or dicyclohexylamine. The salt that separated was filtered off, washed, and recrystallised, if necessary, from a suitable solvent. The alkyldinitro-phenol was obtained by

²⁸ A. H. M. Kirby, E. L. Frick, L. D. Hunter, and R. P. Tew, *Nitrocompounds, Proc. Intern. Symp. Warsaw (1963)*, Pergamon Press, London, 1964, p. 483.

acidifying with concentrated hydrochloric acid a solution of the salt in acetone or methanol, filtering the solution from the amine hydrochloride, where necessary, removing the solvent from the filtrate on the steam-bath under reduced pressure, dissolving the residue in petroleum, washing the solution with water, drying (Na_2SO_4), and removing the solvent on the steam-bath at 2 mm. The alkyldinitro-phenols were obtained as yellow, brown, or red oils. Tables 11 and 12 summarise the preparation and physical data of the 2-alkyl-4,6-dinitro- and 4-alkyl-2,6-dinitro-phenols.

Spectroscopic Measurements.—The i.r.²⁹ and n.m.r.³⁰ measurements were conducted as described previously.

We thank Dr. J. E. Page for the i.r. and n.m.r. spectra.

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²⁹ J. E. Page and S. E. Staniforth, *J. Chem. Soc.*, 1962, 1292.

³⁰ G. F. H. Green, J. E. Page, and S. E. Staniforth, *J. Chem. Soc.*, 1964, 144.