STRUCTURES AND PESTICIDAL ACTIVITIES OF DERIVATIVES OF DINITROPHENOLS

VIII.*—Effects of substitution with C_5 to C_{13}-s-alkyl groups and of esterification on the acaricidal activity of dinitrophenols

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38 methyl-, 37 ethyl- and 19 other alkyl-carbonates, 37 crotonates, 10 acrylates and 17 other esters, and 15 methyl ethers of 2-(C_5 to C_{13}-s-alkyl)-4,6-dinitro- and 4-(C_4 to C_{13}-s-alkyl)-2,6-dinitrophenols were synthesised, and their activities against *Tetranychus telarius* (greenhouse red spider mite) were investigated. 2-s-Alkyl-4,6-dinitrophenols and esters were more active than their 4-s-alkyl-2,6-dinitro- analogues, acaricidal activity remaining high with the 4,6-dinitrophenols up to 2-(C_{11}-s-alkyl). Generally compactness of the 2-s-alkyl group aided activity. Methyl ethers had very low activity. Esters of 2-(C_3 to C_7-s-alkyl)-4,6-dinitrophenols were more acaricidal than the parent phenols, but the reverse was the case with C_8 to C_{13}-s-alkyl compounds. Crotonates and other esters were generally less active than methyl carbonates. The methyl carbonates of 2-(1-ethylhexyl)- and 2-(1-propylpentyl)-4,6-dinitrophenols were found to be of particular economic interest as acaricides.

Introduction

In Part I[1] the acaricidal activity of dinitrophenols and their carbonates was examined and in Part III[2] that of dinitro-*m*-cresols and their carbonates with nuclear normal and α-methyl alkyl groups containing up to five carbon atoms was examined. High activity was given by phenols and *m*-cresols containing nitro-groups in the 4- and 6-positions and an alkyl group with an α-methyl substituent in the 2-position.

In a series of ethyl carbonates of 2-alkyl-4,6-dinitrophenols, the C_3-alkyl (isopropyl) compounds showed moderate activity, the C_4-alkyl (s-butyl and t-butyl) and C_5-alkyl (1-methylbutyl) compounds high activity, and the C_8-alkyl (1-methylheptyl) ones lower activity.[3,4]

4-s-Butyl- and 4-t-butyl-2,6-dinitrophenols[1] and their carbonates[1] and 4-s-butyl-5-methyl-2,6-dinitrophenyl carbonates[2] had low to moderate activity.

The effects on acaricidal activity of size, shape and position of the alkyl groups containing 5 to 13 carbon atoms in 2-alkyl-4,6-dinitro- and 4-alkyl-2,6-dinitrophenols and the effect of their esterification and etherification have been examined.

Experimental

Derivation of compounds

Chloroformates

All the chloroformates used here have been described in the literature. Methyl-, ethyl- and isopropyl-chloroformates were obtained commercially. Methyl thiolo-, propyl-, butyl-, s-butyl-, isobutyl-, hexyl-, octyl-, 1-methylheptyl- and decyl-chloroformates were prepared by the method described in Part I.[1]

Acid chlorides

These were prepared by methods described in the literature.

Phenols

2-Isopropyl-4,6-dinitrophenol (Compound No. 220), 2-s-butyl-4,6-dinitrophenol (No. 1), 4-s-butyl-2,6-dinitrophenol (No. 108) and 2-(1-methylbutyl)-4,6-dinitrophenol (No. 4) have been described in the literature. The compounds shown in Table I were prepared as described in Part IV.[5]

TABLE I

Compounds prepared as described in Part IV[5]

2-(1-R)-4,6-dinitrophenols		4-(1-R)-2,6-dinitrophenols	
Compound no.	R	Compound no.	R
7	ethylpropyl	111	methylbutyl
10	methylpentyl	112	ethylpropyl
13	ethylbutyl	115	methylpentyl
16	methylhexyl	116	ethylbutyl
19	ethylpentyl	119	methylhexyl
22	propylbutyl	122	ethylpentyl
25	methylheptyl	125	propylbutyl
30	ethylhexyl	126	methylheptyl
37	propylpentyl	131	ethylhexyl
40	methyloctyl	144	propylpentyl
43	ethylheptyl	149	methyloctyl
46	propylhexyl	152	ethylheptyl
49	butylpentyl	155	propylhexyl
52	ethyloctyl	158	butylpentyl
55	propylheptyl	160	ethyloctyl
58	butylhexyl	163	propylheptyl
61	propyloctyl	166	butylhexyl
64	butylheptyl	169	methyldecyl
67	pentylhexyl	170	ethylnonyl
70	pentylheptyl	171	propyloctyl
73	hexylheptyl	172	butylheptyl
		175	pentylhexyl
		176	ethyldecyl
		177	propylnonyl
		178	butyloctyl
		179	pentylheptyl
		180	propyldecyl
		181	butylnonyl
		182	pentyloctyl
		183	hexylheptyl

*Part VII, *J. chem. Soc.*, (c), 1967, 2618.

TABLE II

2-Alkyl-4,6-dinitrophenyl carbonates

No. of compound	Alkyl	Carbonate	M.p.	Appearance and n_D^{20} of oil or appearance of solid	Formula	Found: N, %	Required: N, %
8	1-Ethylpropyl	Methyl	66–69°	Orange pink crystals	$C_{13}H_{16}N_2O_7$	9·3	9·0
9	1-Ethylpropyl	Ethyl	43–46°	Orange pink crystals	$C_{14}H_{18}N_2O_7$	8·9	8·6
11	1-Methylpentyl	Methyl		Yellow, 1·5222	$C_{14}H_{18}N_2O_7$	8·6	8·6
12	1-Methylpentyl	Ethyl		Yellow, 1·5170	$C_{15}H_{20}N_2O_7$	8·4	8·2
14	1-Ethylbutyl	Methyl[a]	52·5–54°	Off-white prisms	$C_{14}H_{18}N_2O_7$	8·8	8·6
15	1-Ethylbutyl	Ethyl		Yellow, 1·5177	$C_{15}H_{20}N_2O_7$	8·0	8·2
17	1-Methylhexyl	Methyl		Yellow, 1·5197	$C_{15}H_{20}N_2O_7$	8·6	8·2
18	1-Methylhexyl	Ethyl		Yellow, 1·5145	$C_{16}H_{22}N_2O_7$	8·2	7·9
20	1-Ethylpentyl	Methyl		Yellow, 1·5210	$C_{15}H_{20}N_2O_7$	7·9	8·2
21	1-Ethylpentyl	Ethyl		Yellow, 1·5151	$C_{16}H_{22}N_2O_7$	7·9	7·9
23	1-Propylbutyl	Methyl	57–58°	Brown crystals	$C_{15}H_{20}N_2O_7$	8·6	8·2
24	1-Propylbutyl	Ethyl		Pale brown, 1·5137	$C_{16}H_{22}N_2O_7$	7·8	7·9
26	1-Methylheptyl	Methyl		Yellow, 1·5159	$C_{16}H_{22}N_2O_7$	7·9	7·9
27	1-Methylheptyl	Ethyl		Yellow, 1·5120	$C_{17}H_{24}N_2O_7$	7·5	7·6
28	1-Methylheptyl	Isopropyl		Yellow, 1·5075	$C_{18}H_{26}N_2O_7$	7·3	7·3
29	1-Methylheptyl	Methyl thiolo-		Yellow, 1·5404	$C_{16}H_{22}N_2O_6S$	7·6	7·6
31	1-Ethylhexyl	Methyl		Yellow, 1·5170	$C_{16}H_{22}N_2O_7$	7·8	7·9
32	1-Ethylhexyl	Ethyl		Yellow, 1·5133	$C_{17}H_{24}N_2O_7$	7·6	7·6
33	1-Ethylhexyl	Propyl		Orange, 1·5100	$C_{18}H_{26}N_2O_7$	7·2	7·3
34	1-Ethylhexyl	Isopropyl		Orange, 1·5088	$C_{18}H_{26}N_2O_7$	6·7	7·3
35	1-Ethylhexyl	Hexyl		Orange, 1·5041	$C_{21}H_{32}N_2O_7$	6·9	6·6
36	1-Ethylhexyl	Decyl		Orange, 1·4951	$C_{25}H_{40}N_2O_7$	5·8	5·8
38	1-Propylpentyl	Methyl[b]	66–68°	Fine white needles	$C_{16}H_{22}N_2O_7$	8·2	7·9
39	1-Propylpentyl	Ethyl		Red-brown, 1·514	$C_{17}H_{24}N_2O_7$	7·5	7·6
41	1-Methyloctyl	Methyl		Light red, 1·5139	$C_{17}H_{24}N_2O_7$	8·0	7·6
42	1-Methyloctyl	Ethyl		Light red, 1·5100	$C_{18}H_{26}N_2O_7$	7·6	7·3
44	1-Ethylheptyl	Methyl		Light red, 1·5159	$C_{17}H_{24}N_2O_7$	7·9	7·6
45	1-Ethylheptyl	Ethyl		Yellow, 1·5112	$C_{18}H_{26}N_2O_7$	6·5	7·3
47	1-Propylhexyl	Methyl		Orange, 1·5142	$C_{17}H_{24}N_2O_7$	7·5	7·6
48	1-Propylhexyl	Ethyl		Orange, 1·5098	$C_{18}H_{26}N_2O_7$	7·2	7·3
50	1-Butylpentyl	Methyl	47–48°	Cream coloured crystals	$C_{17}H_{24}N_2O_7$	7·8	7·6
51	1-Butylpentyl	Ethyl		Light red, 1·5112	$C_{18}H_{26}N_2O_7$	7·3	7·3
53	1-Ethyloctyl	Methyl		Yellow, 1·5128	$C_{18}H_{26}N_2O_7$	7·4	7·3
54	1-Ethyloctyl	Ethyl		Yellow, 1·5092	$C_{19}H_{28}N_2O_7$	7·2	7·1
56	1-Propylheptyl	Methyl		Yellow, 1·5134	$C_{18}H_{26}N_2O_7$	7·5	7·3
57	1-Propylheptyl	Ethyl		Yellow, 1·5094	$C_{19}H_{28}N_2O_7$	7·5	7·1
59	1-Butylhexyl	Methyl		Pale brown, 1·5123	$C_{18}H_{26}N_2O_7$	7·3	7·3
60	1-Butylhexyl	Ethyl		Pale brown, 1·5082	$C_{19}H_{28}N_2O_7$	6·9	7·1
62	1-Propyloctyl	Methyl		Yellow, 1·5102	$C_{19}H_{28}N_2O_7$	6·9	7·1
63	1-Propyloctyl	Ethyl		Yellow, 1·5071	$C_{20}H_{30}N_2O_7$	6·7	6·8
65	1-Butylheptyl	Methyl		Brown, 1·5112	$C_{19}H_{28}N_2O_7$	6·8	7·1
66	1-Butylheptyl	Ethyl		Brown, 1·5072	$C_{20}H_{30}N_2O_7$	7·3	6·8
68	1-Pentylhexyl	Methyl		Yellow, 1·5100	$C_{19}H_{28}N_2O_7$	6·6	7·1
69	1-Pentylhexyl	Ethyl		Yellow, 1·5063	$C_{20}H_{30}N_2O_7$	6·7	6·8
71	1-Pentylheptyl	Methyl		Yellow, 1·5087	$C_{20}H_{30}N_2O_7$	7·2	6·8
72	1-Pentylheptyl	Ethyl		Yellow, 1·5051	$C_{21}H_{32}N_2O_7$	6·8	6·6
74	1-Hexylheptyl	Methyl		Orange-yellow, 1·5069	$C_{21}H_{32}N_2O_7$	6·9	6·6
75	1-Hexylheptyl	Ethyl		Orange-yellow, 1·5048	$C_{22}H_{34}N_2O_7$	6·6	6·4

4-(1,1,3,3-Tetramethylbutyl)-2,6-dinitrophenol (Compound No. 147). A mixture of commercial *p*-t-octylphenol [described as containing 94% 4-(1,1,3,3-tetramethylbutyl)phenol] (20·6 g; 0·1 mole), ethylene dichloride (37 ml) and nitric acid (36%; 48 ml) was heated under reflux for 1·5 h. The organic layer was separated and washed thoroughly with 3% aqueous sodium sulphate. The yellow solid, m.p. 112–113°, that separated out after each washing was filtered off. Ethylene dichloride was then removed from the organic layer leaving a dark oil which was dissolved in light petroleum, b.p. 60–80°, then shaken with 20% aqueous sodium carbonate. The red solid that separated was filtered off, dissolved in hot water and acidified. The oil that separated was extracted with light petroleum, b.p. 40–60°, treated with charcoal and anhydrous sodium sulphate and filtered. The solid that was obtained on adding cyclohexylamine was filtered off. The *cyclohexylamine salt* of the phenol melts at 215° (from aqueous propan-2-ol). When a solution of the salt in methanol was acidified with conc. hydrochloric acid the *phenol* was obtained as light brown prisms, m.p. 50–51° (from methanol) (Found: N, 9·5. $C_{14}H_{20}N_2O_5$ requires N, 9·4%.)

Dinitrophenyl carbonates

The general method of preparation was essentially as described in Part I.[1] Alkyl dinitrophenol, in acetone, and potassium carbonate (1·1 equivalent), were heated under reflux for 1 h. The chloroformate (1·1 equivalent) was then added and the mixture was heated under reflux for 3 h. The solid was filtered off and washed with acetone. The volatile matter was then removed from the combined filtrate and washings on a steam-bath at 10–20 mm pressure. The residue was dissolved in benzene or light petroleum, washed

with 1% aqueous sodium carbonate and then with water. The organic layer was separated, dried (sodium sulphate) and the solvent was removed on the steam-bath at 1–2 mm pressure. When appropriate the residue was crystallised from a suitable solvent. The oils were not distilled. Yields ranged from 80 to 100%. The physical data of the carbonates are shown in Tables II and III.

2-s-Butyl-4,6-dinitrophenyl methyl and ethyl carbonates (Compounds Nos. 2 & 3), 2-(1-methylbutyl)-4,6-dinitrophenyl methyl and ethyl carbonates (Nos. 5 & 6) and 2-isopropyl-4,6-dinitrophenyl ethyl carbonate (No. 221) were prepared as described in Part I.[1]

Dinitrophenyl esters

The general method of preparation was essentially as described in Part VI.[6] Alkyldinitrophenol, in acetone, and potassium carbonate (1·1 equivalent) were heated under reflux for 1 h. To the stirred ice salt-cooled mixture the acid chloride (1·1 equivalent) was slowly added. The mixture was kept stirred at 0–5° for a further hour, allowed to stand for 16 h at room temp., then heated under reflux for 3 h. The solid was then filtered off and washed with acetone, and the combined filtrate and washings were worked up in the same way as the carbonates. When appropriate the residue was crystallised from a suitable solvent. The oils were not distilled. Yields ranged from 80 to 100% and were generally higher for the compounds with unsaturated ester chains. Yields of compounds with saturated ester chains could be improved by adding, after one hour's heating, a further 0·1 equivalent of potassium carbonate, then 0·1 equivalent of the acid chloride and proceeding as described above. The physical data of the esters are shown in Tables IV and V.

TABLE III

4-Alkyl-2,6-dinitrophenyl carbonates

No. of compound	Alkyl	Carbonate	M.p.	Appearance and $n_D^{20°}$ of oil or appearance of solid	Formula	Found: N, %	Required: N, %
109	s-Butyl	Methyl[c,d]	59·5–60°	Off-white prisms	$C_{12}H_{14}N_2O_7$	9·1	9·4
110	s-Butyl	Ethyl	33–34°	Brown crystals	$C_{13}H_{16}N_2O_7$	9·1	9·0
113	1-Ethylpropyl	Methyl[c]	66°	Cream coloured prisms	$C_{13}H_{16}N_2O_7$	9·4	9·0
114	1-Ethylpropyl	Ethyl		Yellow, 1·5183	$C_{14}H_{18}N_2O_7$	8·8	8·6
117	1-Ethylbutyl	Methyl		Red-brown, 1·5210	$C_{14}H_{18}N_2O_7$	8·3	8·6
118	1-Ethylbutyl	Ethyl		Red-brown, 1·5155	$C_{15}H_{20}N_2O_7$	8·2	8·2
120	1-Methylhexyl	Methyl		Brown, 1·5172	$C_{15}H_{20}N_2O_7$	8·0	8·2
121	1-Methylhexyl	Ethyl		Red-brown, 1·5131	$C_{16}H_{22}N_2O_7$	7·8	7·9
123	1-Ethylpentyl	Methyl		Gold coloured, 1·5188	$C_{15}H_{20}N_2O_7$	8·1	8·2
124	1-Ethylpentyl	Ethyl		Orange, 1·5148	$C_{16}H_{22}N_2O_7$	8·2	7·9
127	1-Methylheptyl	Methyl		Pale brown, 1·5129	$C_{16}H_{22}N_2O_7$	8·0	7·9
128	1-Methylheptyl	Ethyl		Pale brown, 1·5070	$C_{17}H_{24}N_2O_7$	7·7	7·6
129	1-Methylheptyl	Isopropyl		Yellow, 1·5040	$C_{18}H_{22}N_2O_7$	7·3	7·3
130	1-Methylheptyl	Methyl thiolo-		Pale brown, 1·5360 (n_D^{24})	$C_{16}H_{22}N_2O_6S$	7·6	7·6
132	1-Ethylhexyl	Methyl		Yellow, 1·5133 (n_D^{20})	$C_{16}H_{22}N_2O_7$	7·4	7·9
133	1-Ethylhexyl	Ethyl		Orange, 1·5084 (n_D^{24})	$C_{17}H_{24}N_2O_7$	7·8	7·6
134	1-Ethylhexyl	Propyl		Orange-brown, 1·5068	$C_{18}H_{26}N_2O_7$	7·3	7·3
135	1-Ethylhexyl	Isopropyl		Dark brown, 1·5062 (n_D^{20})	$C_{18}H_{26}N_2O_7$	7·4	7·3
136	1-Ethylhexyl	Butyl		Brown, 1·5049	$C_{19}H_{28}N_2O_7$	7·1	7·1
137	1-Ethylhexyl	s-Butyl		Orange, 1·5030	$C_{19}H_{28}N_2O_7$	7·0	7·1
138	1-Ethylhexyl	Isobutyl		Orange-brown, 1·5035	$C_{19}H_{28}N_2O_7$	6·9	7·1
139	1-Ethylhexyl	Hexyl		Orange-red 1·5012	$C_{21}H_{32}N_2O_7$	6·9	6·6
140	1-Ethylhexyl	Octyl		Orange, 1·4930	$C_{23}H_{36}N_2O_7$	6·2	6·2
141	1-Ethylhexyl	1-Methylheptyl		Orange, 1·4927	$C_{23}H_{36}N_2O_7$	6·7	6·2
142	1-Ethylhexyl	Decyl		Orange, 1·4926	$C_{25}H_{40}N_2O_7$	5·8	5·8
143	1-Ethylhexyl	Methyl thiolo-[d]	56–58°	Pale green prisms	$C_{16}H_{22}N_2O_6S$	7·6	7·6
145	1-Propylpentyl	Methyl		Orange, 1·5131	$C_{16}H_{22}N_2O_7$	7·9	7·9
146	1-Propylpentyl	Ethyl		Orange, 1·4995	$C_{17}H_{24}N_2O_7$	7·8	7·6
148	't-Octyl'*	Isopropyl[d]	57–58°	Cream prisms	$C_{18}H_{26}N_2O_7$	7·2	7·3
150	1-Methyloctyl	Methyl		Yellow, 1·5108	$C_{17}H_{24}N_2O_7$	7·9	7·6
151	1-Methyloctyl	Ethyl		Yellow, 1·5050	$C_{18}H_{26}N_2O_7$	6·9	7·3
153	1-Ethylheptyl	Methyl		Red-brown, 1·5136	$C_{17}H_{24}N_2O_7$	7·3	7·6
154	1-Ethylheptyl	Ethyl		Red-brown, 1·5091	$C_{18}H_{26}N_2O_7$	7·0	7·3
156	1-Propylhexyl	Methyl		Orange-red, 1·5126	$C_{17}H_{24}N_2O_7$	7·8	7·6
157	1-Propylhexyl	Ethyl		Orange-red, 1·5085	$C_{18}H_{26}N_2O_7$	7·4	7·3
159	1-Butylpentyl	Methyl	40–42°	Brown crystals	$C_{17}H_{24}N_2O_7$	8·1	7·6
161	1-Ethyloctyl	Methyl		Yellow, 1·5094	$C_{18}H_{26}N_2O_7$	6·7	7·3
162	1-Ethyloctyl	Ethyl		Yellow, 1·5054	$C_{19}H_{28}N_2O_7$	6·7	7·1
164	1-Propylheptyl	Methyl		Yellow, 1·5088	$C_{18}H_{26}N_2O_7$	7·5	7·3
165	1-Propylheptyl	Ethyl		Yellow, 1·5050	$C_{19}H_{28}N_2O_7$	7·1	7·1
167	1-Butylhexyl	Methyl		Yellow, 1·5102	$C_{18}H_{26}N_2O_7$	7·3	7·3
168	1-Butylhexyl	Ethyl		Yellow, 1·5063	$C_{19}H_{28}N_2O_7$	7·0	7·1
173	1-Butylheptyl	Methyl		Yellow, 1·5078	$C_{19}H_{28}N_2O_7$	7·5	7·1
174	1-Butylheptyl	Ethyl		Yellow, 1·5038	$C_{20}H_{30}N_2O_7$	6·8	6·8
184	1-Hexylheptyl	Methyl		Yellow, 1·5040	$C_{21}H_{32}N_2O_7$	6·6	6·6
185	1-Hexylheptyl	Ethyl		Yellow, 1·5009	$C_{22}H_{34}N_2O_7$	5·8	6·4

*Substantially 1,1,3,3-tetramethylbutyl

2-s-Butyl-4,6-dinitrophenyl crotonate (No. 76) and 2-(1-methylbutyl)-4,6-dinitrophenyl crotonate (No. 77) were prepared as described in Part VI.[6]

Dinitrophenyl methyl ethers

The method of preparation was essentially as described in Part I.[1] The potassium dinitrophenoxide (0·01 mole) was dehydrated by addition of toluene (20 ml) and then removal of toluene (10 ml) and any water present by distillation. Dimethyl sulphate (0·011 mole) was then added and the mixture was heated under reflux (oil-bath) for 6 h and occasionally shaken. It was cooled to room temp. and shaken with 10% aqueous sodium hydroxide (4 × 10 ml), then with water (2 × 10 ml). The organic layer was separated and treated with sodium sulphate and charcoal. The solvent was then removed (steam-bath) at 0·2 mm. The alkyldinitroanisoles were obtained as orange-brown or reddish brown oils in 82–93% yields. Lower yields were obtained when the reaction mixtures were heated under reflux for shorter times. No apparent methylation occurred when the potassium dinitrophenoxide was heated with methyl iodide in acetone under reflux for 1 h. The physical data of the anisoles are shown in Table VI.

Formulation of compounds

The compounds were formulated as 10–25% w/v emulsifiable concentrates in a suitable non-phytotoxic solvent (such as heavy naphtha) and emulsifier. The solutions were then diluted with water to the required concentrations.

Biological Results

The tests were carried out as described in Part I.[1]

Results from the different biological tests would be expected to be comparable and valid, since the tests were carried out over a short period of time.

The results are presented in Tables VII–XI. For completeness, the activity of the crotonates of 2-alkyl-4,6-dinitro- and 4-alkyl-2,6-dinitro-phenols is included in Table IX. The results obtained with carbonates other than methyl- and ethyl-carbonates are presented in Table X.

2-(1-Ethylhexyl)- and 2-(1-propylpentyl)-4,6-dinitrophenyl methyl carbonates

The differences in acaricidal activity of the three isomeric phenols of the C_8-alkyl series (Nos. 25, 30, 37) were not significant. Esterification of 2-(1-methylheptyl)-4,6-dinitrophenol to the methyl- (No. 26) or ethyl- (No. 27) carbonates, acrylate (No. 89) or crotonate (No. 90) (Tables VII & IX, Fig. 2), of 2-(1-ethylhexyl)-4,6-dinitrophenol (No. 30) to the ethyl carbonate (No. 32), butyrate (No. 92), acrylate (No. 93) or crotonate (No. 94) (Tables VII & IX, Fig. 3), and of 2-(1-propylpentyl)-4,6-dinitrophenol (No. 37) to the crotonate (No. 95) (Table VII) reduced the acaricidal activity of the phenols. However, esterification of 2-(1-ethylhexyl)- and 2-(1-propylpentyl)4,6-dinitrophenols to the methyl carbonates (No. 38) either had little effect on activity (No. 31) or brought about an increase in acaricidal activity (Table VII). 2-Alkyl-4,6-dinitrophenyl methyl carbonates were generally less phytotoxic than the parent phenols. 2-(1-Ethylhexyl)- and 2-(1-propylpentyl)-4,6-dinitrophenyl methyl carbonates thus combine high acaricidal activity with low phytotoxicity.[8] In extensive laboratory testing a mixture consisting substantially of the two methyl carbonates gave rapid kills of the motile stages of *Tetranychus telarius*, specially selected for its resistance to organophosphate insecticides. In field

TABLE IV

2-Alkyl-4,6-dinitrophenyl esters

No. of compound	Alkyl	Ester	Appearance and n_D^{20} of oil	Formula	Found: N, %	Required: N, %
78	1-Ethylpropyl	Crotonate	Orange, 1·5432	$C_{15}H_{18}N_2O_6$	8·8	8·7
79	1-Methylpentyl	Acetate	Pale green, 1·5261	$C_{14}H_{18}N_2O_6$	9·3	9·0
80	1-Methylpentyl	Acrylate	Pale green, 1·5362	$C_{15}H_{18}N_2O_6$	9·0	8·7
81	1-Methylpentyl	Crotonate	Yellow, 1·5352	$C_{16}H_{20}N_2O_6$	8·0	8·3
82	1-Ethylbutyl	Crotonate	Orange-yellow, 1·5386	$C_{16}H_{20}N_2O_6$	7·9	8·3
83	1-Methylhexyl	Acetate	Pale green, 1·5211	$C_{15}H_{20}N_2O_6$	8·4	8·6
84	1-Methylhexyl	Acrylate	Pale yellow, 1·5332	$C_{16}H_{20}N_2O_6$	8·4	8·3
85	1-Methylhexyl	Crotonate	Yellow, 1·5328	$C_{17}H_{22}N_2O_6$	7·6	8·0
86	1-Ethylpentyl	Crotonate	Yellow, 1·5350	$C_{17}H_{22}N_2O_6$	8·1	8·0
87	1-Propylbutyl	Crotonate	Yellow, 1·5304	$C_{17}H_{22}N_2O_6$	7·6	8·0
88	1-Methylheptyl	Acetate	Yellow, 1·5195	$C_{16}H_{22}N_2O_6$	8·5	8·3
89	1-Methylheptyl	Acrylate	Yellow, 1·5278	$C_{17}H_{22}N_2O_6$	8·2	8·0
90	1-Methylheptyl	Crotonate	Yellow, 1·5306	$C_{18}H_{24}N_2O_6$	7·5	7·7
91	1-Ethylhexyl	Acetate	Orange, 1·5216	$C_{16}H_{22}N_2O_6$	8·3	8·3
92	1-Ethylhexyl	Butyrate	Orange, 1·5160	$C_{18}H_{26}N_2O_6$	7·7	7·6
93	1-Ethylhexyl	Acrylate	Pale brown, 1·5295	$C_{17}H_{22}N_2O_6$	7·6	8·0
94	1-Ethylhexyl	Crotonate	Yellow, 1·5282	$C_{18}H_{24}N_2O_6$	7·7	7·7
95	1-Propylpentyl	Crotonate	Red-brown, 1·5330	$C_{18}H_{24}N_2O_6$	7·7	7·7
96	1-Methyloctyl	Crotonate	Pale brown, 1·5249	$C_{19}H_{26}N_2O_6$	7·3	7·4
97	1-Ethylheptyl	Crotonate	Pale red, 1·5283	$C_{19}H_{26}N_2O_6$	6·9	7·4
98	1-Propylhexyl	Crotonate	Orange, 1·5241	$C_{19}H_{26}N_2O_6$	6·9	7·4
99	1-Butylpentyl	Crotonate	Pale red, 1·5278	$C_{19}H_{26}N_2O_6$	7·5	7·4
100	1-Ethyloctyl	Crotonate	Yellow, 1·5234	$C_{20}H_{28}N_2O_6$	6·6	7·1
101	1-Propylheptyl	Crotonate	Yellow, 1·5253	$C_{20}H_{28}N_2O_6$	7·1	7·1
102	1-Butylhexyl	Crotonate	Yellow, 1·5260	$C_{20}H_{28}N_2O_6$	6·9	7·1
103	1-Propyloctyl	Crotonate	Yellow, 1·5220	$C_{21}H_{30}N_2O_6$	7·1	6·9
104	1-Butylheptyl	Crotonate	Pale brown, 1·5236	$C_{21}H_{30}N_2O_6$	7·4	6·9
105	1-Pentylhexyl	Crotonate	Yellow, 1·5214	$C_{21}H_{30}N_2O_6$	6·9	6·9
106	1-Pentylheptyl	Crotonate	Dark yellow, 1·5181	$C_{22}H_{32}N_2O_6$	6·7	6·7
107	1-Hexylheptyl	Crotonate	Orange-yellow, 1·5162	$C_{23}H_{34}N_2O_6$	6·6	6·5

TABLE V

4-Alkyl-2,6-dinitrophenyl esters

No. of compound	Alkyl	Ester	M.p.	Appearance and n_D^{20} of oil or appearance of solid	Formula	Found: N, %	Required: N, %
186	s-Butyl	Crotonate[c,d]	65°	Cream prisms	$C_{14}H_{16}N_2O_6$	8·7	9·1
187	1-Ethylpropyl	Crotonate		Yellow, 1·5394	$C_{15}H_{18}N_2O_6$	8·8	8·7
188	1-Ethylbutyl	Crotonate		Red-brown, 1·5370	$C_{16}H_{20}N_2O_6$	7·7	8·3
189	1-Methylhexyl	Crotonate		Yellow, 1·5257	$C_{17}H_{22}N_2O_6$	8·3	8·4
190	1-Ethylpentyl	Crotonate		Orange, 1·5236	$C_{17}H_{22}N_2O_6$	7·7	8·0
191	1-Propylbutyl	Acetate[e]	60–61°	White needles	$C_{15}H_{20}N_2O_6$	8·6	8·6
192	1-Propylbutyl	Acrylate		Yellow, 1·5284	$C_{16}H_{20}N_2O_6$	8·2	8·3
193	1-Methylheptyl	Acrylate		Yellow, 1·5255	$C_{17}H_{22}N_2O_6$	8·1	8·0
194	1-Methylheptyl	Crotonate		Pale brown, 1·5236	$C_{18}H_{24}N_2O_6$	7·7	7·7
195	1-Ethylhexyl	Acetate[e]	51·5–53°	Yellow prisms	$C_{16}H_{22}N_2O_6$	8·5	8·3
196	1-Ethylhexyl	Butyrate		Yellow, 1·5110	$C_{18}H_{26}N_2O_6$	7·5	7·6
197	1-Ethylhexyl	Isobutyrate		Red-brown, 1·5100	$C_{18}H_{26}N_2O_6$	7·7	7·6
198	1-Ethylhexyl	Octanoate		Red-brown, 1·5040	$C_{22}H_{34}N_2O_6$	6·4	6·6
199	1-Ethylhexyl	Chloroacetate		Pale brown, 1·5278	$C_{16}H_{27}ClN_2O_6$	7·5	7·5
200	1-Ethylhexyl	2-Chloropropionate		Orange-brown, 1·5202	$C_{17}H_{23}ClN_2O_6$	Cl, 9·7 N, 7·0	Cl, 9·2 N, 7·2
201	1-Ethylhexyl	3-Chloropropionate		Orange-brown, 1·5243	$C_{17}H_{23}ClN_2O_6$	Cl, 9·6 N, 6·9	Cl, 9·2 N, 7·2
202	1-Ethylhexyl	Acrylate		Orange, 1·5220	$C_{17}H_{22}N_2O_6$	8·0	8·0
203	1-Ethylhexyl	Crotonate		Yellow, 1·5250	$C_{18}H_{24}N_2O_6$	7·6	7·7
204	1-Ethylhexyl	Methacrylate	44–45°	Cream coloured crystals	$C_{18}H_{24}N_2O_6$	7·5	7·7
205	1-Ethylhexyl	3-Methylcrotonate		Orange-brown, 1·5297	$C_{19}H_{26}N_2O_6$	7·4	7·4
206	1-Ethylhexyl	Benzoate		Brown, 1·5585	$C_{21}H_{24}N_2O_6$	7·0	7·0
207	1-Ethylhexyl	*p*-Chlorobenzoate		Orange, 1·5604	$C_{21}H_{23}ClN_2O_6$	Cl, 8·1 N, 6·3	Cl, 8·2 N, 6·4
208	1-Propylpentyl	Crotonate		Dark orange, 1·5272	$C_{18}H_{24}N_2O_6$	7·3	7·7
209	1-Methyloctyl	Crotonate		Yellow, 1·5229	$C_{19}H_{26}N_2O_6$	7·2	7·4
210	1-Ethylheptyl	Crotonate		Red-brown, 1·5255	$C_{19}H_{26}N_2O_6$	7·3	7·4
211	1-Propylhexyl	Crotonate		Orange-red, 1·5240	$C_{19}H_{26}N_2O_6$	7·3	7·4
212	1-Ethyloctyl	Acrylate		Orange, 1·5197	$C_{19}H_{26}N_2O_6$	7·8	7·4
213	1-Ethyloctyl	Crotonate		Yellow, 1·5210	$C_{20}H_{28}N_2O_6$	6·8	7·1
214	1-Propylheptyl	Acrylate		Orange, 1·5200	$C_{19}H_{26}N_2O_6$	7·5	7·4
215	1-Propylheptyl	Crotonate		Yellow, 1·5216	$C_{20}H_{28}N_2O_6$	7·4	7·1
216	1-Butylhexyl	Acrylate		Yellow, 1·5202	$C_{19}H_{26}N_2O_6$	7·5	7·4
217	1-Butylhexyl	Crotonate		Pale yellow, 1·5211	$C_{20}H_{28}N_2O_6$	7·2	7·1
218	1-Butylheptyl	Crotonate		Yellow, 1·5201	$C_{21}H_{30}N_2O_6$	7·1	6·9
219	1-Hexylheptyl	Crotonate		Yellow, 1·5152	$C_{23}H_{24}N_2O_6$	6·6	6·4

Solvents for crystallisation used for certain compounds in Tables II–V:
[a] light petroleum, b.p. 40–60°; [b] propan-2-ol; [c] ethanol; [d] methanol; [e] light petroleum, b.p. 60–80°

TABLE VI

2-Alkyl-4,6-dinitrophenyl methyl ethers

No. of compound	Alkyl	n_D^{20}	Formula	Found: N, %	Required: N, %
222	1-Methylheptyl*	1·5303	$C_{15}H_{22}N_2O_5$	9·2	9·0
223	1-Ethylhexyl*	1·5298	$C_{15}H_{22}N_2O_5$	8·9	9·0
224	1-Propylpentyl*	1·5324	$C_{15}H_{22}N_2O_5$	9·1	9·0
225	1-Ethylheptyl	1·5273	$C_{16}H_{24}N_2O_5$	8·8	8·6
226	1-Propylhexyl	1·5282	$C_{16}H_{24}N_2O_5$	8·8	8·6
227	1-Butylpentyl	1·5798	$C_{16}H_{24}N_2O_5$	8·7	8·6
228	1-Hexylheptyl	1·516	$C_{20}H_{32}N_2O_5$	7·3	7·4
		4-Alkyl-2,6-dinitrophenyl methyl ethers			
229	1-Ethylpentyl	1·5246	$C_{14}H_{20}N_2O_5$	9·6	9·5
230	1-Methylheptyl*	1·5206	$C_{15}H_{22}N_2O_5$	9·3	9·0
231	1-Ethylhexyl*	1·5225	$C_{15}H_{22}N_2O_5$	9·1	9·0
232	1-Propylpentyl*	1·5222	$C_{15}H_{22}N_2O_5$	8·9	9·0
233	1-Methyloctyl	1·5184	$C_{16}H_{24}N_2O_5$	9·0	8·6
234	1-Propylhexyl	1·5190	$C_{16}H_{24}N_2O_5$	9·0	8·6
235	1-Butylpentyl	1·515	$C_{16}H_{24}N_2O_5$	9·2	8·6
236	1-Butyloctyl	1·5215	$C_{19}H_{30}N_2O_5$	7·9	7·7

*Clifford, Watkins and Woodcock[9] referred to the compound, but did not report its preparation, physical data or analysis

TABLE VII

Contact acaricidal activity of 2-alkyl-4,6-dinitrophenols, their methyl- and ethyl-carbonates and their crotonates

Alkyl	No. of carbon atoms in alkyl group	Phenols					Methyl carbonates					Ethyl carbonates					Crotonates				
		No. of compound	Kill of *T. telarius* (%) at ppm				No. of compound	Kill of *T. telarius* (%) at ppm				No. of compound	Kill of *T. telarius* (%) at ppm				No. of compound	Kill of *T. telarius* (%) at ppm			
			100	30	10	3		100	30	10	3		100	30	10	3		100	30	10	3
Isopropyl	3	220	99	34	30	–	–	–	–	–	–	221	98	80	75	–	–	–	–	–	–
s-Butyl	4	1	100	50	35	–	2	100	100	98	56	3	100	100	99	96	76	100	100	97	95
1-Methylbutyl	5	4	100	70	65	–	5	100	100	100	91	6	100	100	99	99	77	100	100	100	91
1-Ethylpropyl	5	7	100	100	92	65	8	100	100	96	37	9	100	100	100	95	78	100	100	100	99
1-Methylpentyl	6	10	100	96	59	–	11	100	98	80	61	12	100	89	83	–	81	100	81	61	–
1-Ethylbutyl	6	13	100	100	73	–	14	100	100	98	69	15	100	99	99	79	82	100	100	100	98
1-Methylhexyl	7	16	99	75	47	–	17	99	95	78	–	18	99	75	58	–	85	94	65	70	–
1-Ethylpentyl	7	19	65	53	36	–	20	92	84	81	–	21	98	83	57	–	86	99	74	70	–
1-Propylbutyl	7	22	100	100	91	53	23	100	100	98	81	24	100	100	92	56	87	100	95	85	–
1-Methylheptyl	8	25	99	99	87	33	26	81	78	61	–	27	96	57	38	–	90	73	59	23	–
1-Ethylhexyl	8	30	100	100	88	58	31	100	94	73	61	32	96	80	60	–	94	85	74	38	9
1-Propylpentyl	8	37	100	100	61	–	38	99	100	98	57	39	100	95	83	–	95	92	79	69	–
1-Methyloctyl	9	40	100	100	90	38	41	100	71	52	–	42	78	55	47	–	96	80	64	35	–
1-Ethylheptyl	9	43	100	83	61	–	44	72	32	38	–	45	47	38	39	–	97	40	29	20	–
1-Propylhexyl	9	46	100	100	99	52	47	100	97	92	84	48	100	90	58	–	98	84	49	47	–
1-Butylpentyl	9	49	100	100	92	77	50	100	86	84	60	51	100	92	29	–	99	64	40	51	–
1-Ethyloctyl	10	52	100	56	48	–	53	57	0	0	–	54	40	40	38	–	100	44	0	0	–
1-Propylheptyl	10	55	100	100	85	74	56	87	70	40	–	57	87	75	40	–	101	45	24	24	–
1-Butylhexyl	10	58	100	100	96	87	59	87	80	45	–	60	77	56	38	41	102	59	40	36	–
1-Propyloctyl	11	61	100	100	86	–	62	80	60	54	–	63	77	46	24	–	103	60	39	21	–
1-Butylheptyl	11	64	100	90	61	–	65	67	70	49	–	66	33	17	12	–	104	66	39	37	–
1-Pentylhexyl	11	67	100	100	84	77	68	88	66	35	–	69	74	73	67	–	105	39	40	36	–
1-Pentylheptyl	12	70	90	77	57	–	71	52	0	0	–	72	44	29	24	–	106	61	49	34	–
1-Hexylheptyl	13	73	100	84	55	–	74	26	32	16	–	75	24	13	–	–	107	16	12	3	–

TABLE VIII

Contact acaricidal activity of 4-alkyl-2,6-dinitrophenols, their methyl- and ethyl-carbonates and their crotonates

Alkyl	No. of carbon atoms in alkyl group	Phenols					Methyl carbonates					Ethyl carbonates					Crotonates				
		No. of compound	Kill of *T. telarius* (%) at ppm				No. of compound	Kill of *T. telarius* (%) at ppm				No. of compound	Kill of *T. telarius* (%) at ppm				No. of compound	Kill of *T. telarius* (%) at ppm			
			300	100	30	10		300	100	30	10		300	100	30	10		300	100	30	10
s-Butyl	4	108	–	55	43	39	109	57	58	42	43	110	44	40	32	23	186	89	64	29	–
1-Methylbutyl	5	111	72	36	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Ethylpropyl	5	112	–	14	3	–	113	–	55	48	45	114	–	49	29	–	187	–	82	71	66
1-Methylpentyl	6	115	76	43	39	29	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Ethylbutyl	6	116	65	58	50	41	117	52	42	36	27	118	47	30	28	–	188	77	60	50	18
1-Methylhexyl	7	119	92	54	39	–	120	63	55	–	–	121	65	37	–	–	189	79	67	42	–
1-Ethylpentyl	7	122	95	86	71	–	123	65	43	51	–	124	54	53	47	–	190	61	50	45	–
1-Propylbutyl	7	125	90	33	28	28	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Methylheptyl	8	126	57	46	44	–	127	67	32	34	–	128	45	25	18	–	194	28	29	15	–
1-Ethylhexyl	8	131	92	43	36	–	132	42	36	18	–	133	32	18	–	–	203	67	61	36	–
1-Propylpentyl	8	144	62	35	38	36	145	26	31	33	–	146	48	49	42	33	208	41	36	36	34
't-Octyl'	8	147	–	66	44	25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Methyloctyl	9	149	66	59	38	20	150	56	–	–	–	151	46	–	–	–	209	87	–	–	–
1-Ethylheptyl	9	152	96	79	51	–	153	45	66	46	–	154	80	66	42	–	210	54	37	29	–
1-Propylhexyl	9	155	98	67	55	29	156	25	0	0	0	157	60	65	23	11	211	44	16	11	2
1-Butylpentyl	9	158	89	71	34	33	159	45	37	36	20	–	–	–	–	–	–	–	–	–	–
1-Ethyloctyl	10	160	–	46	45	45	161	81	–	–	–	162	82	–	–	–	213	69	–	–	–
1-Propylheptyl	10	163	97	–	–	–	164	74	–	–	–	165	46	–	–	–	215	56	–	–	–
1-Butylhexyl	10	166	83	50	14	2	167	46	18	20	14	168	36	18	18	15	217	45	36	26	15
1-Methyldecyl	11	169	67	55	44	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Ethylnonyl	11	170	77	57	46	40	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Propyloctyl	11	171	75	57	52	38	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Butylheptyl	11	172	84	–	–	–	173	37	–	–	–	174	56	–	–	–	218	50	–	–	–
1-Pentylhexyl	11	175	81	33	37	36	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Ethyldecyl	12	176	91	55	49	54	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Propylnonyl	12	177	81	62	59	61	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Butyloctyl	12	178	54	66	40	51	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Pentylheptyl	12	179	69	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Propyldecyl	13	180	84	56	59	38	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Butylnonyl	13	181	78	51	41	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Pentyloctyl	13	182	74	56	51	48	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1-Hexylheptyl	13	183	–	52	38	35	184	–	45	37	0	185	–	24	13	–	219	–	38	27	–

TABLE IX

Contact acaricidal activity of certain 2-alkyl-4,6-dinitrophenyl esters (I) and 4-alkyl-2,6-dinitrophenyl esters (II)

Alkyl	No. of carbon atoms in alkyl group	Ester	No. of compound (I)	Kill of *T. telarius* (%) at ppm 300	100	30	10	3	No. of compound (II)	Kill of *T. telarius* (%) at ppm 300	100	30	10
s-Butyl	4	Crotonate	76	–	100	100	97	95	186	89	64	29	–
1-Ethylpropyl	5	Crotonate	78	–	100	100	100	99	187	–	82	71	66
1-Methylpentyl	6	Acetate	79	100	100	100	100	86	–	–	–	–	–
1-Methylpentyl		Acrylate	80	100	100	100	100	84	–	–	–	–	–
1-Methylpentyl		Crotonate	81	–	100	81	61	–	–	–	–	–	–
1-Ethylbutyl	6	Crotonate	82	–	100	100	100	98	188	77	60	50	18
1-Methylhexyl	7	Acetate	83	100	100	100	98	73	–	–	–	–	–
1-Methylhexyl		Acrylate	84	100	100	96	97	–	–	–	–	–	–
1-Methylhexyl		Crotonate	85	–	94	65	70	–	189	79	67	42	–
1-Ethylpentyl	7	Crotonate	86	–	99	74	70	–	190	61	50	45	–
1-Propylbutyl	7	Acetate	–	–	–	–	–	–	191	80	40	32	–
1-Propylbutyl		Acrylate	–	–	–	–	–	–	192	88	–	58	56
1-Propylbutyl		Crotonate	87	–	100	95	85	–	–	–	–	–	–
1-Methylheptyl	8	Acetate	88	100	100	94	88	–	–	–	–	–	–
1-Methylheptyl		Acrylate	89	96	40	–	–	–	193	61	58	32	8
1-Methylheptyl		Crotonate	90	–	73	59	23	–	194	28	29	15	–
1-Ethylhexyl	8	Acetate	91	–	100	96	95	–	195	13	10	3	0
1-Ethylhexyl		Butyrate	92	–	88	87	44	–	196	51	35	24	24
1-Ethylhexyl		Isobutyrate	–	–	–	–	–	–	197	42	27	27	0
1-Ethylhexyl		Octanoate	–	–	–	–	–	–	198	60	45	40	30
1-Ethylhexyl		Chloroacetate	–	–	–	–	–	–	199	59	32	21	–
1-Ethylhexyl		2-Chloropropionate	–	–	–	–	–	–	200	82	53	36	–
1-Ethylhexyl		3-Chloropropionate	–	–	–	–	–	–	201	21	–	11	–
1-Ethylhexyl		Acrylate	93	100	95	51	38	–	202	36	24	15	7
1-Ethylhexyl		Crotonate	94	–	85	74	38	9	203	67	61	36	–
1-Ethylhexyl		Methacrylate	–	–	–	–	–	–	204	40	32	32	31
1-Ethylhexyl		3-Methyl crotonate	–	–	–	–	–	–	205	71	62	55	–
1-Ethylhexyl		Benzoate	–	–	–	–	–	–	206	32	32	30	29
1-Ethylhexyl		*p*-Chlorobenzoate	–	–	–	–	–	–	207	36	29	7	–
1-Propylpentyl	8	Crotonate	95	–	92	79	69	–	208	41	36	36	34
1-Methyloctyl	9	Crotonate	96	–	80	64	35	–	209	87	–	–	–
1-Ethylheptyl	9	Crotonate	97	–	40	29	20	–	210	54	37	29	–
1-Propylhexyl	9	Crotonate	98	–	84	49	47	–	211	44	16	11	2
1-Ethyloctyl	10	Acrylate	–	–	–	–	–	–	212	65	35	21	–
1-Ethyloctyl		Crotonate	100	–	44	0	0	–	213	69	–	–	–
1-Propylheptyl	10	Acrylate	–	–	–	–	–	–	214	39	36	32	–
1-Propylheptyl		Crotonate	101	–	45	24	24	–	215	56	–	–	–
1-Butylhexyl	10	Acrylate	–	–	–	–	–	–	216	22	34	18	–
1-Butylhexyl		Crotonate	102	–	59	40	36	–	217	45	36	26	15
1-Butylheptyl	11	Crotonate	104	–	66	38	37	–	218	50	–	–	–
1-Hexylheptyl	13	Crotonate	107	–	16	12	3	–	219	–	38	27	–

TABLE X

Contact acaricidal activity of certain carbonates of 2-alkyl-4,6-dinitrophenols (III) and carbonates of 4-alkyl-2,6-dinitrophenols (IV)

Alkyl	No. of carbon atoms in alkyl group	Carbonate	No. of compound (III)	Kill of *T. telarius* (%) at ppm 300	100	30	10	3	No. of compound (IV)	Kill of *T. telarius* (%) at ppm 300	100	30	10
1-Methylheptyl	8	Isopropyl	28	49	38	21	24	–	129	33	34	16	11
1-Methylheptyl		Methyl thiolo-	29	93	63	46	33	–	130	47	38	36	–
1-Ethylhexyl	8	Propyl	33	–	95	61	45	–	134	66	30	10	–
1-Ethylhexyl		Isopropyl	34	–	100	87	57	–	135	29	0	9	–
1-Ethylhexyl		Butyl	–	–	–	–	–	–	136	38	39	33	25
1-Ethylhexyl		s-Butyl	–	–	–	–	–	–	137	34	33	34	16
1-Ethylhexyl		Isobutyl	–	–	–	–	–	–	138	37	8	14	–
1-Ethylhexyl		Hexyl	35	–	100	99	26	–	139	29	22	–	–
1-Ethylhexyl		Octyl	–	–	–	–	–	–	140	22	26	–	–
1-Ethylhexyl		1-Methylheptyl	–	–	–	–	–	–	141	88	52	51	33
1-Ethylhexyl		Decyl	36	–	96	92	15	–	142	37	37	39	29
1-Ethylhexyl		Methyl thiolo-	–	–	–	–	–	–	143	38	23	23	–
't-Octyl'	8	Isopropyl	–	–	–	–	–	–	148	13 (59% at 1000 ppm)			

TABLE XI

Contact acaricidal activity of certain 2-alkyl-4,6-dinitrophenols and 4-alkyl-2,6-dinitrophenols and their methyl ethers

Alkyl	No. of carbon atoms in alkyl group	Phenols			Methyl ethers		
		No. of compound	Kill of *T. telarius* (%) at ppm 300	100	No. of compound	Kill of *T. telarius* (%) at ppm 300	100
2-Alkyl-4,6-dinitrophenols and their methyl ethers							
1-Methylheptyl	8	25	100	99	222	30	15
1-Ethylhexyl	8	30	100	100	223	45	34
1-Propylpentyl	8	37	100	100	224	57	34
1-Ethylheptyl	9	43	100	100	225	32	32
1-Propylhexyl	9	46	100	100	226	44	20
1-Butylpentyl	9	49	100	100	227	30	33
1-Hexylheptyl	13	73	100	100	228	20	17
4-Alkyl-2,6-dinitrophenols and their methyl ethers							
1-Ethylpentyl	7	122	95	86	229	16	18
1-Methylheptyl	8	126	57	46	230	31	26
1-Ethylhexyl	8	131	92	43	231	42	26
1-Propylpentyl	8	144	62	35	232	37	17
1-Methyloctyl	9	149	66	59	233	35	29
1-Propylhexyl	9	155	98	67	234	41	27
1-Butylpentyl	9	158	89	71	235	42	31
1-Butyloctyl	12	178	54	66	236	52	26

trials the mixture at 250–500 ppm gave rapid kills of active stages of red spider mites: *Panonychus ulmi* on apples, pears, and peaches; *Tetranychus telarius* on beans; and *Tetranychus urticae* on beans, egg plants, vines, and chrysanthemums.

Mammalian toxicity

The acute oral toxicity to rats was determined as follows. The compounds were suspended in distilled water with 25% propylene glycol and 0·5% Tween 80 to give a 300 mg/ml concentration. Thirty female Wistar rats (bodyweight 140–170 g) were used per determination. The doses were administered by stomach tube. Mortalities were observed after 7 days. Median lethal doses are presented in Table XII.

TABLE XII

Toxicity to rats of certain alkyldinitrophenyl esters
2,4,6-RR′.$C_6H_2(NO_2)$.O.CO.R″

No. of compound	R	R′	R″	Acute oral LD_{50} mg/kg
26	1-Methylheptyl	NO_2	OCH_3	1400
31	1-Ethylhexyl	NO_2	OCH_3	> 3000
38	1-Propylpentyl	NO_2	OCH_3	> 3000
127	NO_2	1-Methylheptyl	OCH_3	> 3000
132	NO_2	1-Ethylhexyl	OCH_3	1750
202	NO_2	1-Ethylhexyl	$CH{:}CH_2$	1075
145	NO_2	1-Propylpentyl	OCH_3	1800

Discussion

Nuclear substitution in phenols

In Part I[1,3] it was reported that 2-s-butyl- and 2-t-butyl-4,6-dinitrophenols and their aliphatic carbonates had much higher acaricidal activity than 4-s-butyl- and 4-t-butyl-2,6-dinitrophenols and corresponding carbonates. For maximum acaricidal activity phenols required nitro-groups in the 4- and 6-positions and an s-alkyl group in the 2-position. The present investigation using s-alkyldinitrophenols with C_5 to C_{13}-s-alkyl groups confirms this postulate since these 2-s-alkyl-4,6-dinitrophenols and their esters were much more active against *Tetranychus telarius* adults than the corresponding 4-s-alkyl-2,6-dinitrophenols and their esters (Tables VII–X), with the notable exception of the 1-ethylpentyl-dinitrophenols (Nos. 19, 122).

An examination of the activity of the 2-s-alkyl-4,6-dinitrophenols (Table VII) shows that in the C_5-, C_6-, C_7- (except for the ethylpentyl-isomer, No. 19) and C_{10}-alkyl series the more compact the s-alkyl group the higher the activity (Nos. 4 & 7; 10 & 13; 16 & 22; 52, 55 & 58). In the C_8-alkyl series the ethylhexyl- (No. 30) was only marginally more active than the methylheptyl-isomer (No. 25) (cf. Kirby *et al.*[7]). In the C_9-alkyl series the more compact propylhexyl- (No. 46) and butylpentyl- (No. 49) isomers were more active than were the methyloctyl- (No. 40) and ethylheptyl- (No. 43) isomers. Activity was still high at C_{11}-alkyl (Nos. 61, 64, 67), and dropped at C_{12}- (No. 70) and C_{13}- (No. 73) alkyl.

Except for 2-(1-methylalkyl)- the plots of the activity of 2-(1-ethylalkyl)-, 2-(1-propylalkyl)- and 2-(1-butylalkyl)-4,6-dinitrophenols at 10 ppm against *T. telarius* adults show a maximum when the alkyl was a hexyl group (Fig. 1).

The ester chain

In Part I[1] it was reported that the toxicity to spider mites of alkyl carbonates of 2-s-butyl- and 2-(1-methylbutyl)-4,6-dinitrophenols was higher than that of the parent phenols. It was assumed that the un-ionised carbonates penetrated more readily to the vital sites of action, thus yielding a greater concentration of the toxicants in the organism. Activity was considered to be due to the hydrolytic products, i.e. the alkyldinitrophenols. Figs. 2–5 show comparisons of percentage mortalities of *T. telarius* adults caused by concentrations of 10 ppm 2-s-alkyl-4,6-dinitrophenols, their methyl carbonates, ethyl carbonates and crotonates. With 1-methyl-

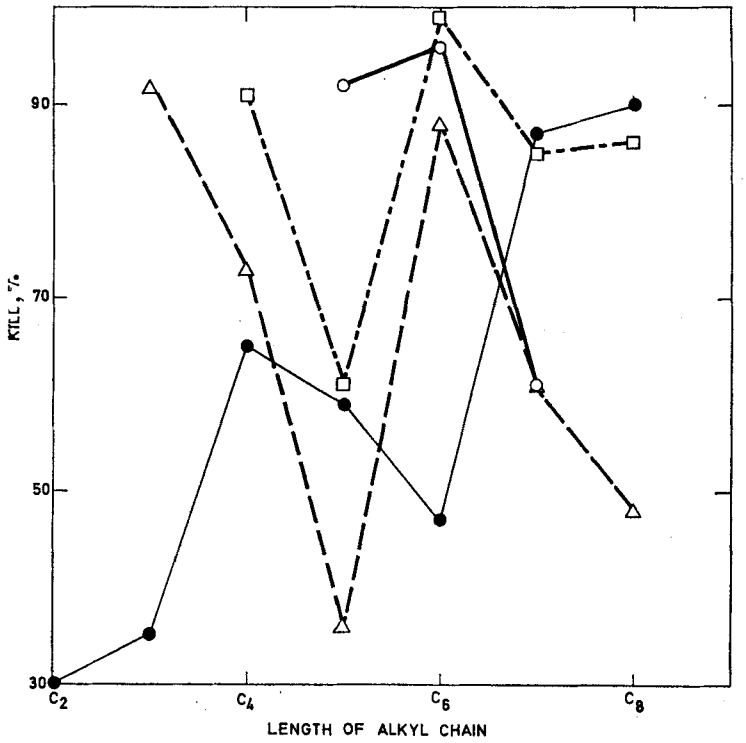


FIG. 1. *Activity of some* 2-(1-*Me, Et, Pr or Bu alkyl*)-4,6-*dinitrophenols at* 10 *ppm against* Tetranychus telarius *adults*
●——● 1-Methylalkyl △- - - - -△ 1-Ethylalkyl □—·—·—□ 1-Propylalkyl ○——○ 1-Butylalkyl

alkyl-compounds (Fig. 2) up to 1-methylhexyl- (total chain of 7 carbon atoms), with 1-ethylalkyl-compounds (Fig. 3) up to 1-ethylpentyl- (total chain of 7 carbon atoms), with 1-propyl-alkyl-compounds (Fig. 4) up to 1-propylpentyl- (total chain of 8 carbon atoms) the esters were more active than the phenols. With the longer alkyl chains: heptyl and octyl (Fig. 2); hexyl (except for No. 31), heptyl and octyl (Fig. 3); hexyl, heptyl and octyl (Fig. 4) and pentyl, hexyl and heptyl with 1-butylalkyl-compounds (Fig. 5) the phenols were more active than their ester derivatives. High polarity of 2-(C_3 to C_7-alkyl)-4,6-dinitrophenols may impede their penetration to the vital sites of action; esterification may aid it. The more lipophilic properties of 2-(C_8 to C_{13}-alkyl)-4,6-dinitrophenols may aid their penetration and render these phenols more active. Esterification of these higher alkylphenols proved detrimental to activity perhaps because: increase in bulk may interfere with penetration; and the bulky alkyl group may hinder hydrolysis of the esters to the phenols. Significantly, the bulkier crotonates of 4,6-dinitrophenols with 2-s-alkyl groups of seven or more carbon atoms were less active than the corresponding methyl carbonates (Table VII, Figs 2–5),

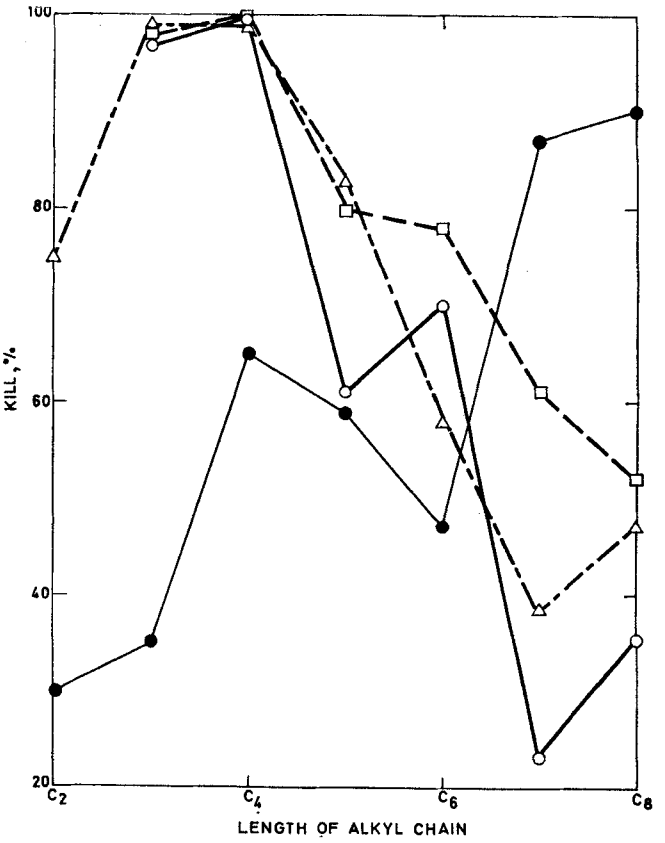


FIG. 2. (right). *Activity of* 2-(1-*methylalkyl*)-4,6-*dinitrophenols, their methyl carbonates, ethyl carbonates and crotonates at* 10 *ppm against* Tetranychus telarius *adults*

●——● Phenols
□- - - - -□ Methyl carbonates
△—·—·—△ Ethyl carbonates
○——○ Crotonates

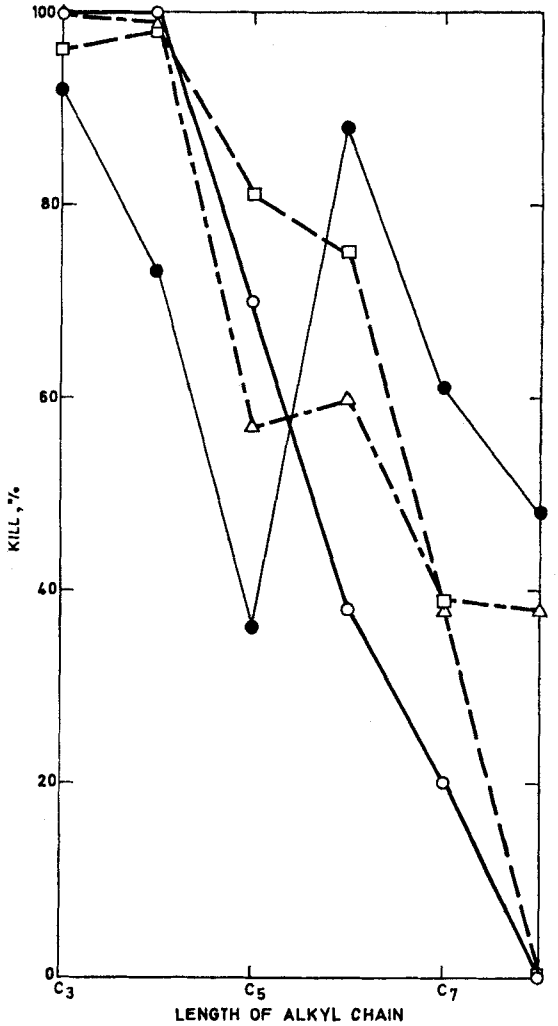
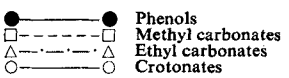


FIG. 3. *Activity of* 2-(1-*ethylalkyl*)-4,6-*dinitrophenols, their methyl carbonates, ethyl carbonates and crotonates at* 10 *ppm against* Tetranychus telarius *adults*



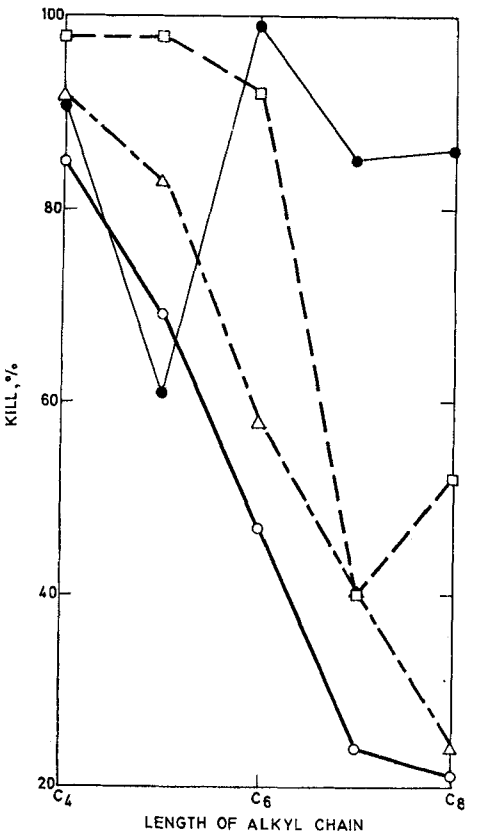
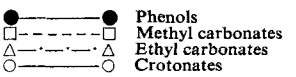


FIG. 4. *Activity of* 2-(1-*propylalkyl*)-4,6-*dinitrophenols, their methyl carbonates, ethyl carbonates and crotonates at* 10 *ppm against* Tetranychus telarius *adults*



the crotonates were less active than the acetates (Table IX; Nos. 81 & 79; 85 & 83; 90 & 88; 94 & 91), and 2-(1-ethylhexyl)-4,6-dinitrophenyl butyrate (No. 92) was less active than the acetate (No. 91).

Extension of the carbonate chain of 2-(1-ethylhexyl)-4,6-dinitrophenol (Table X) to propyl (No. 33) and isopropyl (No. 34), hexyl (No. 35) and decyl (No. 36) had surprisingly little effect on activity. 2-(1-Methylheptyl)-4,6-dinitrophenyl isopropyl- (No. 28) and methylthiolo- (No. 29) carbonates were considerably less active than methyl- (No. 26) or ethyl- (No. 27) carbonates.

As with the 2-s-alkyl-4,6-dinitrophenols, esterification generally reduced the activity of 4-s-alkyl-2,6-dinitrophenols containing an s-alkyl group of seven or more carbon atoms (Tables VIII–X).

Etherification

The activity of methyl ethers of 2-alkyl-4,6-dinitro- and 4-alkyl-2,6-dinitro-phenols was found to be very low, compared with that of the parent phenols (Table XI). 2-s-Butyl- and 2-t-butyl-4,6-dinitroanisoles[1] and 2-t-butyl-5-methyl-4,6-dinitroanisole[2] also had very low activity, compared with that of the parent phenols. The view that the low activity of anisoles may be due to their hydrolytic stability[1] gains thus a broader basis.

Conclusions

The following tentative conclusions may be drawn about the structure-activity relationship in the dinitroalkylphenols and their esters examined: 2-s-alkyl-4,6-dinitrophenols are more toxic than 4-s-alkyl-2,6-dinitrophenols to spider mites; with s-alkyl groups whose total number of carbon atoms is 5, 6, 7, 9 or 10 within a series of 2-s-alkyl-4,6-dinitrophenols containing the same total number of carbon atoms, the more compact the isomers the higher is their acaricidal activity; acaricidal activity remains high up to 2-(C_{11}-s-alkyl)-4,6-dinitrophenols, beyond which it drops; generally esters of 2-(C_3 to C_7-s-alkyl)-4,6-dinitrophenols are more acaricidal

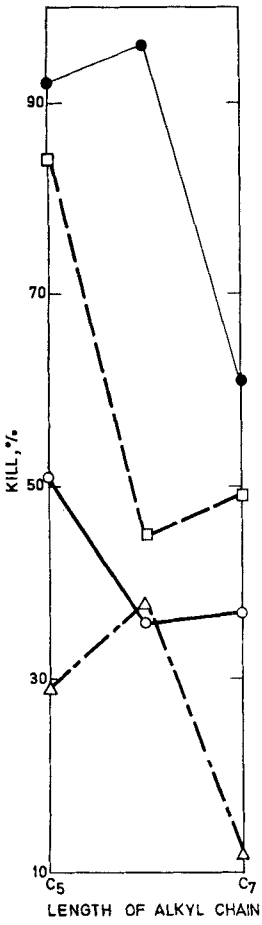


FIG. 5. *Activity of* 2-(1-*butylalkyl*)-4,6-*dinitrophenols, their methyl carbonates, ethyl carbonates and crotonates at* 10 *ppm against* Tetranychus telarius *adults*

Phenols
Methyl carbonates
Ethyl carbonates
Crotonates

than the parent phenols, but 2-(C_8 to C_{13}-s-alkyl)-4,6-dinitrophenols are more acaricidal than their esters, and a similar relationship holds for 4-s-alkyl-2,6-dinitrophenols and their esters; crotonates of 2-(C_7 to C_{13}-s-alkyl)-4,6-dinitrophenols are less acaricidal than methyl carbonates or acetates; 2-s-alkyl-4,6-dinitrophenols are more phytotoxic than their esters; etherification of the toxiphoric phenols substantially reduces acaricidal activity; and methyl carbonates of 2-(1-ethylhexyl)- and 2-(1-propylpentyl)-4,6-dinitrophenols are of particular practical and economic interest for their activity against various resistant spider mites.

Acknowledgments

Thanks are due to Messrs. W. S. Catling and P. J. Jeffery for the assessment of the acaricidal activity of the compounds, and Mr. T. R. Middleton of Glaxo Laboratories Ltd. for the acute oral LD_{50} determination in rats.

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Received 3 July, 1967

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