None of the procedures tested, however time-consuming or theoretically attractive, gave results more closely correlated with plant growth than those obtained simply by adding excess calcium sulphate to saturate the 2·5 : 1 soil suspensions. With calcium sulphate thus eliminated as a variable, the correlation obtained would depend on experimental accuracy in the laboratory. There is no doubt that 2·5 : 1 suspensions of air-dry soil can be prepared not only more readily, but also more reproducibly, than either saturation extracts or displaced soil solutions. The range of experimental values is, however, restricted by saturation of all extracts with calcium sulphate and the conductivity measurements must be precise. The method also obscures the contribution to salinity made by calcium sulphate at concentrations up to saturation in the soil solution.

These results emphasise how calcium sulphate can complicate the assessment of salinity when using 2·5 : 1 soil suspensions, and also show the correlation between plant growth and salinity as measured by a range of techniques. Other work, including relationships between electrical conductivity measurements in various types of soil suspension and extract, will be reported subsequently.

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STUDIES IN FUNGITOXICITY. III.*—Fungitoxicity of Certain β-Nitrostyrenes and Related Compounds

By M. PIANKA

Several β-nitrostyrenes and related compounds have been tested for fungitoxicity to certain economically important parasitic fungi. The activity depended on ring substitution and was most marked when the ring substituent was a nitro group. Small alkyl groups of 1–5 C on the 2-carbon atom enhanced the activity of these compounds, but with 7 C activity began to decrease and was lost with 11 C.

Introduction

In Parts I[1] and II[2] were described the toxicities of certain carbocyanines (in which $n = 2$) and anilinovinyl quaternaries (in which $n = 1$) containing the conjugated system

$$-\overset{+}{N}R{:}\overset{|}{C}\cdot(CH{:}CH)_n\cdot N<$$

against the spores of *Venturia inaequalis* (Cooke) Wint. ; *Botrytis cinerea* Pers. ; and *Fusarium bulbigenum*, Cooke & Massee, var. *lycopersici* (Brushi) Wollenw.

* Part II : *J. Sci. Fd Agric.*, 1959, **10**, 385

This study was extended to nitrostyrenes,[3] of the general formula $ArCH{:}C(R)\cdot NO_2$, in which an electron-attracting group is attached to the end of the conjugated chain. Also related compounds were tested for fungitoxicity.

The antifungal and antibacterial properties of compounds of this type have been described in a number of papers.[4–17]

Experimental

The compounds now tested are shown in Tables I and II. The syntheses of Compounds nos. 1, 2, 4, 7, 10, 11, 17, 20–24, 25, 27, 31, 32, 34, 35, 37–41 were by methods described in the literature.

Table I

Results of fungitoxicity tests with β-nitrostyrenes

No. of compound	Name of compound	M.p.	Reference	*Venturia*	*Botrytis*	*Fusarium*
				LD_{95} values, p.p.m.		
1	1-Phenyl-2-nitroethylene	57–58°	24	320	650	770
2	1-Phenyl-2-nitroprop-1-ene	64°	28	490	600	>1000
3	1-Phenyl-2-nitrobut-1-ene	(b.p. 100°/0·5 mm.)		560	>1000	>1000
4	1-(4-Methoxyphenyl)-2-nitroethylene	86–87°	20	65	70	70
5	1-(4-Methoxyphenyl)-2-nitroprop-1-ene	46–47°	28	120	285	253
6	1-(4-Methoxyphenyl)-2-nitrobut-1-ene	55–56°		44	260	145
7	1-(4-Chlorophenyl)-2-nitroethylene	111–112°	29	96	94	77
8	1-(4-Chlorophenyl)-2-nitroprop-1-ene	88–89°		80	150	80
9	1-(4-Chlorophenyl)-2-nitrobut-1-ene	76–76·5°		60	300	140
10	1-(4-Nitrophenyl)-2-nitroethylene	201–202°	18	25	150	50
11	1-(4-Nitrophenyl)-2-nitroprop-1-ene	114–115°	19	8	25	20
12	1-(4-Nitrophenyl)-2-nitrobut-1-ene	103·5–104·5°		9	23	30
13	1-(4-Nitrophenyl)-2-nitropent-1-ene	101·5–102·5°		12	12	28
14	1-(4-Nitrophenyl)-2-nitrohept-1-ene	67–68°		21	64	62
15	1-(4-Nitrophenyl)-2-nitronon-1-ene	61·5–62·5°		34	>1000	>1000
16	1-(4-Nitrophenyl)-2-nitrotridec-1-ene	64–65°		>1000	>1000	>1000
17	1-(4-Dimethylaminophenyl)-2-nitroethylene	182–183°	20	27	93	82
18	1-(4-Dimethylaminophenyl)-2-nitroprop-1-ene	123°		140	>1000	470
19	1-(4-Dimethylaminophenyl)-2-nitrobut-1-ene	88–89°		17	>1000	166
20	1-(3-Nitrophenyl)-2-nitroethylene	124·5–125·5°	20	85	74	100
21	1-(3,4-Dimethoxyphenyl)-2-nitroethylene	140°	30	16	46	66
22	1-(3,4-Methylenedioxyphenyl)-2-nitroethylene	160·5–161°	20	17	38	71
23	1-(2,4-Dichlorophenyl)-2-nitroethylene	116°	8	45	19	22
24	1-(4-Nitrophenyl)-2-nitro-2-ethoxycarbonylethylene	72–73°	31	130	110	36

1-*Phenyl-2-nitrobut-1-ene* (Compound no. 3)

Benzaldehyde (42·4 g.), 1-nitropropane (35·6 g.) and 33% w/v solution of ethylamine in ethanol (5·6 g.) were kept at 50–55° for 92 h. The water that formed (5·2 c.c.) was separated and the crude oil dried (sodium sulphate) and fractionated. A pale yellow oil, b.p. 100°/0·5 mm., n_D^{20} 1·5723, was obtained (Found: N, 7·5. $C_{10}H_{11}NO_2$ requires N, 7·5%).

1-(4-*Methoxyphenyl*)-2-*nitrobut*-1-*ene* (Compound no. 6)

Anisaldehyde (24·6 g.), 1-nitropropane (16·2 g.) and n-butylamine (1·5 g.) were kept in a stoppered flask for 14 days. Benzene (20 c.c.) was then added and the solution dried (sodium sulphate) and fractionated. The fraction boiling at 128–158°/0·4 mm. was collected. On

addition of alcohol a solid crystallised out and was separated by filtration. Large lemon-yellow crystals were obtained, m.p. 55–56°, first from carbon tetrachloride and then from ethyl acetate (Found: N, 6·3. $C_{11}H_{13}NO_3$ requires N, 6·8%).

1-(4-*Chlorophenyl*)-2-*nitroprop*-1-*ene* (Compound no. 8)

p-Chlorobenzaldehyde (21 g.), nitroethane (11·3 g.) and n-butylamine (1·1 g.) were kept in a stoppered flask for 14 days. On addition of some alcohol, a solid crystallised out and was separated by filtration. Large lemon-yellow crystals were obtained from alcohol, m.p. 88–89° (Found: N, 7·1. $C_9H_8ClNO_2$ requires N, 7·3%).

Table II

Results of fungitoxicity tests

No. of compound	Name of compound	M.p.	Reference	*Venturia*	*Botrytis*	*Fusarium*
				LD_{95} values, p.p.m.		
	2-Furyl derivatives					
25	1-(2-Furyl)-2-nitroethylene	74–76°	32	>1000	>1000	>1000
26	1-(2-Furyl)-2-nitroprop-1-ene	51–52°		>1000	>1000	>1000
27	1-(5-Nitro-2-furyl)-2-nitroethylene	143–144°	33	33	35	28
	2-Thiophen derivatives					
28	1-(2-Thienyl)-2-nitroethylene	80–80·5°		440	>1000	520
29	1-(2-Thienyl)-2-nitroprop-1-ene	67·5°		445	>1000	245
30	1-(5-Nitro-2-thienyl)-2-nitroprop-1-ene	122·5–123°		22	97	26
	Miscellaneous compounds					
31	1-(4-Methoxyphenyl)-2-chloroethylene	34°	34	>1000	>1000	>1000
32	1-Methoxy-1,3-diphenyl-2,4-dinitrobutane	151–152°	25	3200	>1000	>1000
33	1-Methoxy-1,3-di-(4-nitrophenyl)-2,4-dinitrobutane	112–113°		210	>1000	>1000
34	1-Ethoxy-1,3-diphenyl-2,4-dinitrobutane	156°	25	1500	>1000	>1000
35	1-Methoxy-1-phenyl-2-bromo-2-nitropropane	51–53°	26	90	>1000	>1000
36	1-Methoxy-1-(4-nitrophenyl)-2-bromo-2-nitropropane	170·5–171·5°		30	>1000	>1000
37	2-Nitrobiphenyl	37°		>1000	>1000	>1000
38	4-Nitrobiphenyl	114°		>1000	>1000	>1000
39	4,2′-Dinitrobiphenyl	92°		>1000	>1000	>1000
40	2,2′-Dinitrobiphenyl	119–120°		>1000	>1000	>1000
41	Biphenyl	71°		>1000	>1000	>1000

1-(4-*Chlorophenyl*)-2-*nitrobut*-1-*ene* (Compound no. 9)

This was prepared in the same way as compound no. 8, but with 1-nitropropane (8·9 g.). Pale yellow needles were obtained from carbon tetrachloride and then from ethyl acetate, m.p. 76–76·5° (Found: N, 6·8. $C_{10}H_{10}ClNO_2$ requires N, 6·6%).

1-(4-*Nitrophenyl*)-2-*nitrobut*-1-*ene* (Compound no. 12)

Method A.—A modification of the method of Baker & Wilson[18] and Priebs[19] was used. 1-Phenyl-2-nitrobut-1-ene (44·2 g.) was added to fuming nitric acid (65 c.c.) with stirring for 2 h. below 0°. The mixture was stirred for a further hour below 0°, poured on to crushed ice (1·5 kg.) and water (500 c.c.) and kept stirred for 16 h. The precipitated yellow solid was separated by filtration, washed with water and then methanol and dried in air. The solid was recrystallised from alcohol, carbon tetrachloride, xylene and acetone in that order. Large lemon-yellow crystals were obtained, m.p. 103·5–104·5° (Found: N, 12·9. $C_{10}H_{10}N_2O_4$ requires N, 13·2%).

Method B.—A modification of the methods of Kamlet[20] and Kollonitsch & Vita[21] was used. *p*-Nitrobenzaldehyde (7·6 g.), 1-nitropropane (4·6 g.), n-caproic acid (0·2 g.), piperidine (0·4 c.c.), tributyl borate (11·6 g.) and benzene (100 c.c.) were heated with stirring in a flask to which a Dean & Stark trap was attached. The solution was concentrated, and the crude product that separated was crystallised from carbon tetrachloride and then from methanol, yielding

large lemon-coloured prisms, m.p. 102–103°. They gave no depression of m.p. with the product made by method A.

The 1-nitroalkanes used in the four preparations next described were synthesised from the appropriate alkyl bromides and silver nitrite by the method of Kornblum *et al.*[22]

1-(4-*Nitrophenyl*)-2-*nitropent*-1-*ene* (Compound no. 13)

p-Nitrobenzaldehyde (7·6 g.), 1-nitrobutane (5·2 g.), n-butylamine (0·3 g.) and ethanol (20 c.c.) were refluxed for 14 h. The solution was concentrated, and the crude product that separated on cooling was filtered off and recrystallised from carbon tetrachloride and then from methanol, yielding small yellow crystals, m.p. 101·5–102·5° (Found: N, 11·5. $C_{11}H_{12}N_2O_4$ requires N, 11·9%).

1-(4-*Nitrophenyl*)-2-*nitrohept*-1-*ene* (Compound no. 14)

This was prepared in the same manner as Compound no. 13, but with 1-nitrohexane (6·6 g.). Small straw-coloured crystals were obtained from methanol and then from carbon tetrachloride, m.p. 67–68° (Found: N, 10·2. $C_{13}H_{16}N_2O_4$ requires N, 10·6%).

1-(4-*Nitrophenyl*)-2-*nitronon*-1-*ene* (Compound no. 15)

This was prepared in the same manner as Compound no. 13, but with 1-nitro-octane (8 g.). Straw-coloured plates were obtained from carbon tetrachloride and then from methanol, m.p. 61·5–62·5° (Found: N, 9·8. $C_{15}H_{20}N_2O_4$ requires N, 9·6%).

1-(4-*Nitrophenyl*)-2-*nitrotridec*-1-*ene* (Compound no. 16)

This was prepared in the same manner as Compound no. 13, but with 1-nitrododecane (12·5 g.). Waxy pale yellow plates were obtained from methanol, m.p. 64–65° (Found: N, 7·7. $C_{19}H_{28}N_2O_4$ requires N, 8·0%).

1-(4-*Dimethylaminophenyl*)-2-*nitroprop*-1-*ene* (Compound no. 18)

p-Dimethylaminobenzaldehyde (7·5 g.), nitroethane (3·8 g.) and n-butylamine (0·4 g.) were kept for 2 days. The solid that crystallised out was removed by filtration and recrystallised from benzene, carbon tetrachloride and then ethyl acetate. Glistening brick-red plates were obtained, m.p. 123° (Found: N, 13·8. $C_{11}H_{14}N_2O_2$ requires N, 13·6%).

1-(4-*Dimethylaminophenyl*)-2-*nitrobut*-1-*ene* (Compound no. 19)

This was prepared in the same manner as Compound no. 18, but with 1-nitropropane (4·2 g.). After 11 days the solid that crystallised out was removed by filtration and recrystallised from carbon tetrachloride, ethyl acetate and then methanol. Glistening orange-yellow plates were obtained, m.p. 88–89° (Found: N, 12·4. $C_{12}H_{16}N_2O_2$ requires N, 12·7%).

1-(2-*Furyl*)-2-*nitroprop*-1-*ene* (Compound no. 26)

Freshly distilled furfural (96 g.), nitroethane (75 g.) and 30% w/v solution of methylamine in alcohol (20·3 g.) were kept for 16 h. at 50–55°. The oil was separated from the water of reaction. It solidified on cooling and was recrystallised from alcohol and then carbon tetrachloride to yield yellow crystals, m.p. 51–52° (Found: N, 9·15. $C_7H_7NO_3$ requires N, 9·15%). They resinified to a hard mass on long standing. Attempts were made to nitrate this compound, but a satisfactory product could not be obtained.

1-(2-*Thienyl*)-2-*nitroethylene* (Compound no. 28)

This compound was prepared from 2-thiophenaldehyde[23] (22·4 g.) and nitromethane (12·2 g.) by Worrall's method.[24] Large greenish-yellow rhomboids were obtained from alcohol with the aid of charcoal, carbon tetrachloride and then ethyl acetate, m.p. 80–80·5° (Found: N, 8·7. $C_6H_5NO_2S$ requires N, 9·0%).

An attempt was made to nitrate this compound with fuming nitric acid below −10°. The solid obtained on pouring the nitration mixture on to crushed ice decomposed on attempted purification.

1-(2-*Thienyl*)-2-*nitroprop*-1-*ene* (Compound no. 29)

A mixture of 2-thiophenaldehyde (5·6 g.), nitroethane (3·8 g.) and n-butylamine (0·4 g.) was kept for 11 days. The solid that formed was recrystallised from benzene, carbon tetrachloride and then ethyl acetate. Light brown crystals were obtained, m.p. 67·5° (Found: N, 8·0. $C_7H_7NO_2S$ requires N, 8·3%).

1-(5-*Nitro*-2-*thienyl*)-2-*nitroprop*-1-*ene* (Compound no. 30)

1-(2-Thienyl)-2-nitroprop-1-ene (1·2 g.) was added with stirring for 20 min. to fuming nitric acid (6·5 c.c.) below −8°. The nitration mixture was kept stirred for a further hour below 0° and then poured on to crushed ice. The solid was removed by filtration and dried under reduced pressure. On recrystallisation from acetone light brown crystals were obtained, m.p. 122·5–123° (Found: N, 13·3. $C_7H_6N_2O_4S$ requires N, 13·1%).

1-*Methoxy*-1,3-*di*-(4-*nitrophenyl*)-2,4-*dinitrobutane* (Compound no. 33)

This compound was prepared by the method of Meisenheimer & Heim[25] from 1-(4-nitrophenyl)-2-nitroethylene and sodium methoxide in methanol. After two recrystallisations-from methanol short cream-coloured needles were obtained, m.p. 112–113° (Found: N, 1·4.3 $C_{17}H_{15}N_4O_9$ requires N, 13·4%).

1-*Methoxy*-1-(4-*nitrophenyl*)-2-*bromo*-2-*nitropropane* (Compound no. 36)

This compound was prepared by the procedure of Senkus[26] with 1-(4-nitrophenyl)-2-nitroprop-1-ene, bromine, aqueous sodium hydroxide and methanol. On recrystallisation from benzene colourless prisms were obtained, m.p. 170·5–171·5° (Found: N, 9·0. $C_{10}H_{11}BrN_2O_5$ requires N, 8·8%).

Fungitoxicity tests

All the tests were carried out by the Montgomery–Moore[27] slide germination technique, and the values of LD_{95} were determined against *Venturia*, *Botrytis* and *Fusarium*, as described in Part I.[1]

Results

Table I shows the results of fungitoxicity tests on 24 β-nitrostyrenes. The ones substituted in the ring proved more active than the unsubstituted.

From Table II it is evident that also in the heterocyclic (furyl and thiophen) analogues substitution (in the 5-position) by nitro groups enhanced fungitoxicity. Further, the effect of substitution by nitro groups was not limited to ethylenic compounds; it also operated in the saturated compounds, as can be seen from a comparison of activities against *Venturia* of 1-methoxy-1,3-diphenyl-2,4-dinitrobutane (Compound no. 32; **I**, R^I,R^{III} = Ph; R^{II} = OCH_3) with its nitro derivative (Compound no. 33; **I**, R^I,R^{III} = 4-NO_2·C_6H_4, R^{II} = OCH_3) and of 1-methoxy-1-phenyl-2-bromo-2-nitropropane (Compound no. 35; **II**, R^{IV} = Ph) with its nitro derivative (Compound no. 36; **II**, R^{IV} = 4-NO_2·C_6H_4).

$$R^I{\cdot}CHR^{II}{\cdot}CH(NO_2){\cdot}CHR^{III}{\cdot}CH_2{\cdot}NO_2$$

(I)

$$R^{IV}{\cdot}CH(OCH_3){\cdot}C(CH_3)Br{\cdot}NO_2$$

(II)

Table III shows that, in the β-nitrostyrenes, a different structure–activity relationship holds against certain parasitic and saprophytic fungi.

The effect of lengthening the alkyl chain R^v in the system 4-NO_2·C_6H_4·CH:CR^v·NO_2 on the toxicity to *Venturia* is shown in Fig. 1.

Discussion

Bousquet, Kirby & Searle[4] noted the fungitoxicity of nitroethylenes to the saprophytic

Table III

Comparison of toxicity of β-nitrostyrenes to certain parasitic and saprophytic fungi

No. of compound	Name on compound	*Venturia*	*Botrytis*	*Fusarium*	*Penicillium* lumber moulds	*Aspergillus niger*
		LD_{95} values, p.p.m.			LD_{100} values, p.p.m.*	
1	1-Phenyl-2-nitroethylene	320	650	770	17	17
2	1-Phenyl-2-nitroprop-1-ene	490	600	>1000	31	31
3	1-Phenyl-2-nitrobut-1-ene	560	>1000	>1000	62	62
7	1-(4-Chlorophenyl)-2-nitroethylene	96	94	77	31	62
8	1-(4-Chlorophenyl)-2-nitroprop-1-ene	80	150	80	250	250
4	1-(4-Methoxyphenyl)-2-nitroethylene	65	70	70	62	62
20	1-(3-Nitrophenyl)-2-nitroethylene	85	74	100	150	125
25	1-(2-Furyl)-2-nitroethylene	>1000	>1000	>1000	17	17

* Results obtained by Bousquet *et al.*[4]

fungi *Penicillium* lumber moulds and *Aspergillus niger*. Table III shows that the ring-substituted nitrostyrenes were less toxic to these organisms than the unsubstituted ones: 1-phenyl-2-nitroethylene (Compound no. 1) was much more active than its 3-nitro- (Compound no. 20) or its 4-methoxy-derivative (Compound no. 4). Against the parasitic fungi, *Venturia*, *Botrytis* and *Fusarium*, the ring-substituted compounds were more active. Also 1-(2-furyl)-2-nitroethylene (Compound no. 25), found to be highly active against Aspergillus and Penicillium,[4, 6] proved inactive to *Venturia*, *Botrytis* and *Fusarium*. McGowan *et al.*,[6] with a technique (agar) different from the one used here, found 1-phenyl-2-nitroethylene (Compound no. 1) and 1-(2-furyl)-2-nitroethylene (Compound no. 25) to be active also against the parasitic *Botrytis allii* and *Fusarium graminearum*.

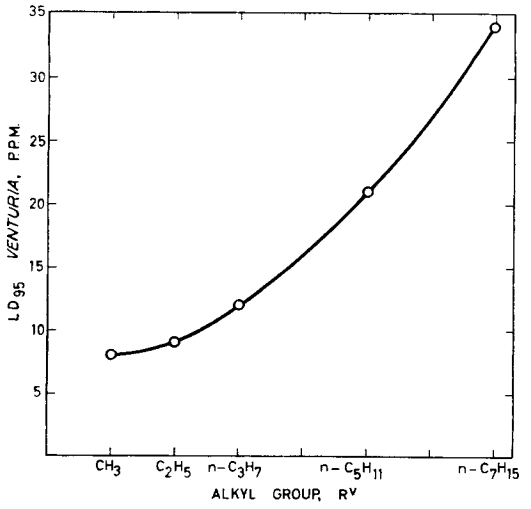

FIG. 1.—*Effect on toxicity to* Venturia, *of lengthening the alkyl chain* R *in the system* $4\text{-}NO_2\cdot C_6H_4\cdot{}^{V}CH{:}CR\cdot NO_2$

The strongly electron-attracting nitro group in the side-chain was found necessary for fungitoxicity. 1-(4-Methoxyphenyl)-2-chloroethylene (Compound no. 31) proved inactive, whereas the 2-nitro-derivative (Compound no. 4) had considerable activity. However, the activity was not limited to the unsaturated compounds. Compounds nos. 35 and 36 (formula **II**), in which the side-chain is fully saturated, possessed good activity against *Venturia*, possibly owing to the reactivity of the bromine towards nucleophilic reagents such as those containing the thiol group.[35, 36]

As already noted, compounds in the nitroethylene series with no substitutents on the rings (nos. 1–3, 25, 26, 28, 29) had poor activity against *Venturia*, *Botrytis* and *Fusarium*. Substitution in the ring enhanced activity. In general, activity increased with increase in

the electronegativity of the substituent and was greatest when the substituent was a nitro group. The effect of substitution by nitro groups was noticeable also in saturated compounds nos. 32 and 33 (formula **I**).

Substitution by an alkyl group on the 2-carbon atom (to which the nitro group is attached) in β-nitrostyrenes, other than those substituted in the ring by a nitro group, had the general effect of lowering the fungitoxicity of the resulting compounds. This may be due to the electron-repelling properties of the alkyl groups counteracting the effect of the 2-nitro group, thus rendering the ethylene bond less reactive to nucleophilic reagents.

That the effect of the alkyl groups is less likely to be of a steric nature is supported by evidence of increased antifungal activity brought about by 2-alkyl substitution in the 1-(4-nitrophenyl)-2-nitroalkene series (Compounds nos. 10–13). The two nitro groups appear to reduce the electronic density on the ethylenic bond to such an extent that it is not materially affected by the electron-donating properties of the alkyl groups, which, as was also found in the carbocyanines[1] and anilinovinyl quaternaries,[2] in fact enhanced the activity (Compounds nos. 10, 11). Had the effect of the 2-alkyl groups been a steric one, the fungitoxicity of this series would have been lowered by substitution with an alkyl group, just as it is in the series in which the ring-substituent is other than a nitro group. The steric effect seems to become operative with the larger alkyl groups (C_7–C_{11}), as shown in Fig. 1.

The introduction of a further electronegative group (—COOEt) (Compound no. 24) does not increase the activity above that of the parent compound.

If in 4,2′-dinitrobiphenyl the 1′,6′-C–C link were broken, a system similar to the one discussed above would obtain. However, 4,2′-dinitrobiphenyl (Compound no. 39) and related compounds proved inactive. For activity it is thus essential that an open chain be available.

Conclusions

On the relationship between fungitoxicity and chemical structure of β-nitrostyrenes and related compounds the following tentative conclusions may perhaps be drawn:

(*a*) substitution in the ring causes an increase in toxicity to the parasitic fungi *Venturia, Botrytis, Fusarium*;

(*b*) increase in activity is paralleled by an increase in the electronegativity of the ring substituent;

(*c*) substitution by an alkyl group on the 2-carbon atom has the effect of lowering the activity, except when the ring substituent is a nitro group;

(*d*) lengthening of the 2-alkyl substituent in 1-(4-nitrophenyl)-2-nitroalkenes reduces the activity;

(*e*) activity against *Venturia* is retained in compounds in which the ethylenic carbon atoms are saturated with bromine and a methoxy group, respectively;

(*f*) if the nitroethylenic chain is part of a conjugated cycle, activity is lost.

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STUDIES IN FUNGITOXICITY. IV.*—Fungitoxicity of Certain Ethylenic Compounds

By J. D. EDWARDS and M. PIANKA

Several benzylidene and related compounds have been tested for fungitoxicity to certain economically important fungi. They were found to be generally less active than β-nitrostyrenes. Certain electron-attracting groups attached to the ethylenic bond conferred activity, but cyano groups did not.

Introduction

In Part III[1] were described the results of tests of a number of β-nitrostyrenes p-R·C_6H_4·CH:CR′·NO_2 and related compounds for toxicity against the spores of *Venturia inaequalis* (Cooke) Wint. ; *Botrytis cinerea* Pers. ; and *Fusarium bulbigenum*, Cooke & Massee, var. *lycopersici* (Brushi) Wollenw. It was considered of interest to prepare and test compounds in which both groups R′ and NO_2 were replaced by electronegative groups, such as COOEt, COR″, CN, and in which the ring substituent was a chlorine atom or a nitro group in different positions.

Roblin & Hechenbleikner[2] observed the insecticidal activity of benzylidene and furfurylidene malonates and McGowan and co-workers[3] noted the fungistatic activity of ethylenic compounds in which one group—COOR, COR, COOH or CHO—was attached to the ethylenic bond.

* Part III : preceding paper