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## THE TOXICITY OF ORGANIC SULPHIDES TO THE EGGS AND LARVAE OF THE GLASSHOUSE RED SPIDER MITE. II.\*

### Miscellaneous Sulphides

By R. F. BROOKES, J. E. CRANHAM, D. GREENWOOD and H. A. STEVENSON

The activities against the eggs and young mites of the glasshouse red spider (*Tetranychus telarius* L.) shown by a number of compounds, all containing two benzene nuclei linked by various sulphur-containing bridges, are tabulated and discussed.

### Introduction

The method used for laboratory testing of a series of SS'-disubstituted alkane- $\alpha\omega$ -dithiols against the red spider mite has already been described.<sup>1</sup> Two of the most active compounds of this series (bisphenylthiomethane and 1:2-bisphenylthioethane) were tested in the field and found to be phytotoxic. The activity against the red spider mite, however, was sufficient to warrant further synthesis of similar compounds in the hope of discovering a non-phytotoxic substance which retained the activity against the mites. All of the compounds tested consisted of two benzene nuclei linked by some variation of the sulphur-containing bridge.

As with the work already described, the present work formed part of a larger programme involving further tests on promisingly active compounds.

### Experimental

#### *Synthesis of compounds*

A. *Benzyl thiolobenzoates*.—This series of compounds was prepared by the action of the appropriate benzoyl chloride on an alkali-metal salt of the substituted phenylmethanethiol.

B. *Disulphides*.—The phenyl disulphides were prepared by oxidation of the corresponding thiols or by reduction of the sulphonyl chlorides, and the benzyl disulphides were obtained from the appropriate benzyl halides and sodium disulphide.

C. *Aryl phenylthioacetates*.—These substances were prepared from the appropriately substituted arylacetyl chlorides and arenethiols in the presence of alkali.

D. *Aryl phenacyl sulphides*.—Similarly obtained by the action of a phenacyl halide on an alkali-metal salt of an arenethiol.

E. *Aryl thiolobenzoates*.—From the benzoyl chloride and arenethiol.

F. *Sulphides*.—The unsymmetrical sulphides were usually prepared from the appropriate thiols and halides but 2-hydroxy-2-phenylethyl phenyl sulphide (Ref. No. 3353) was obtained by the Ponnordorf reduction of phenyl phenacyl sulphide.

G. *Bis-sulphides*.—By the action of the appropriate dihalide on the alkali-metal salt of a thiol.

\* Part I: *J. Sci. Fd Agric.*, 1957, **8**, 31

H. *N*-Benzyl-*N*-methylbenzenesulphenamides.—Prepared by the reaction of an arene-sulphenyl chloride (usually prepared *in situ* by the chlorinolysis of the corresponding disulphide in carbon tetrachloride) with the *N*-methylbenzylamine in the presence of a *tertiary* base (e.g. triethylamine).

#### Biological methods

The methods of rearing mites and of testing have been described in a previous communication.<sup>1</sup> Compounds were first tested by the dipping technique at 0.1% and 0.025% concentration of the test chemical or, with certain compounds, only at 0.1%. A 'formulation control' of suspension medium only, and a 'standard' acaricide were included in each test. Bisphenylthiomethane was used as the standard.

#### Results

Table I gives the initial 'total mortality' (i.e. kill of eggs and young mites) obtained at 0.1% concentration of each compound, and at 0.025% where carried out, corrected by the method of Finney<sup>2</sup> for mortality in the 'formulation controls'. The results of further tests on certain active compounds are summarized in Table II.

#### Discussion of results

The most active groups in laboratory tests were the dibenzyl disulphides and the benzyl thiolobenzoates. No compounds of comparable activity occurred in other groups with the exception of 1:2-dichloro-1:2-bisphenylthioethylene (Ref. No. 2547). The dibenzyl disulphides were more active than the corresponding diphenyl disulphides or the dibenzyl monosulphides.

Table I

A. Benzyl thiolobenzoates											
XC <sub>6</sub> H <sub>4</sub> ·CO·S·CH <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> Y											
Ref. No.	X	Y	% 'Total' mortality		M.p., ° c	Formula	Analysis				Reference
			0.1%	0.025%			Found		Required		
							% C	% H	% C	% H	
2476	H	H	99	76	37-38	C <sub>14</sub> H <sub>12</sub> OS	—	—	—	—	3
2485	H	<i>p</i> -Cl	100	98	42-43	C <sub>14</sub> H <sub>11</sub> OCIS	64.1	4.1	64.1	4.2	*
2477	<i>p</i> -Cl	H	100	92	53-54.5	C <sub>14</sub> H <sub>11</sub> OCIS	63.9	4.4	64.1	4.2	*
2478	<i>p</i> -Cl	<i>p</i> -Cl	92	62	119-120	C <sub>14</sub> H <sub>10</sub> OCl <sub>2</sub> S	56.6	3.4	56.6	3.4	*
								% N		% N	
2699	H	<i>p</i> -NO <sub>2</sub>	49	0	92-92.5	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> NS		5.05		5.1	*
2675	<i>p</i> -NO <sub>2</sub>	H	100	99	83-84	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> NS		5.3		5.1	*
2753	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>	21	0	115-115.5	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> NCIS		4.7		4.6	*
2701	<i>p</i> -NO <sub>2</sub>	<i>p</i> -Cl	7	0	74-75	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> NCIS		4.75		4.6	*

\* Prepared by R. F. B.

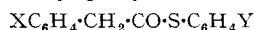
B. Disulphides										
R·S·S·R										
Ref No.	R	% ' Total ' mortality		M.p., ° c or b.p., ° c/mm.	Formula	Analysis				Refer- ence
		0.1%	0.025%			Found		Required		
						% C	% H	% C	% H	
2139	PhCH <sub>2</sub>	99	98	70	C <sub>14</sub> H <sub>14</sub> S <sub>2</sub>	—	—	—	—	4
2462	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> ·CH <sub>2</sub>	99	76	62-63	C <sub>14</sub> H <sub>12</sub> F <sub>2</sub> S <sub>2</sub>	59.75	4.3	59.6	4.3	††
2335	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ·CH <sub>2</sub>	100	66	59	C <sub>14</sub> H <sub>12</sub> Cl <sub>2</sub> S <sub>2</sub>	—	—	—	—	5
2418	PhCH <sub>2</sub> ·CH <sub>2</sub>	97	88	188-192/1.5	C <sub>16</sub> H <sub>18</sub> S <sub>2</sub>	—	—	—	—	6
2013	Ph	43	—	61	C <sub>12</sub> H <sub>10</sub> S <sub>2</sub>	—	—	—	—	7
2463	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	27	—	131/1.0	C <sub>12</sub> H <sub>8</sub> F <sub>2</sub> S <sub>2</sub>	57.0	3.2	56.7	3.15	††
2236	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	52	—	72	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub> S <sub>2</sub>	—	—	—	—	8
2237	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	5	—	87-88	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub> S <sub>2</sub>	—	—	—	—	9
2427	2 : 4 : 5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	0	0	148	C <sub>12</sub> H <sub>4</sub> Cl <sub>6</sub> S <sub>2</sub>	34.7	1.2	33.9	0.9	**
1893	<i>o</i> -AcO·C <sub>6</sub> H <sub>4</sub>	0	—	57	C <sub>18</sub> H <sub>14</sub> O <sub>4</sub> S <sub>2</sub>	57.35	3.8	57.5	4.2	**
4340	3-NO <sub>2</sub> -4-NH <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	5	3	168-169	C <sub>12</sub> H <sub>10</sub> O <sub>4</sub> N <sub>2</sub> S <sub>2</sub>	—	—	—	—	10
2605	C <sub>10</sub> H <sub>7-2</sub>	15	—	139	C <sub>20</sub> H <sub>14</sub> S <sub>2</sub>	—	—	—	—	11

†† Prepared by N. G. Clark.

\*\* Prepared by D. G.

Table I (contd.)

## C. Aryl phenylthioacetates

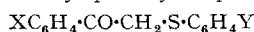


Ref. No.	X	Y	% ' Total ' mortality		M.p., ° c	Formula	Analysis				Reference
							Found		Required		
			0.1 %	0.025 %			% C	% H	% C	% H	
2523	H	H	26	0	34-35	C <sub>14</sub> H <sub>12</sub> OS	73.6	5.2	73.7	5.3	*
2534	H	<i>p</i> -Cl	81	29	62-63	C <sub>14</sub> H <sub>11</sub> OCIS	64.1	4.0	64.0	4.2	*
2639	<i>p</i> -Cl	H	54	12	59.5-60.5	C <sub>14</sub> H <sub>11</sub> OCIS	63.7	4.1	64.0	4.2	*
2679	<i>p</i> -Cl	<i>p</i> -Cl	97	53	63-64	C <sub>14</sub> H <sub>10</sub> OCl <sub>2</sub> S	56.5	3.7	56.6	3.4	*
							% N		% N		
2700	H	<i>p</i> -NO <sub>2</sub>	0	0	69-70	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> NS	5.3		5.1		*
2535	<i>p</i> -NO <sub>2</sub>	H	0	0	61-61	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> NS	5.3		5.1		*
2536	<i>p</i> -NO <sub>2</sub>	<i>p</i> -Cl	P	0	104-105	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> NCIS	4.85		4.55		*
2676	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>	26	0	89-90	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> NCIS	4.7		4.55		*

\* Prepared by R. F. B.

P No assessment due to phytotoxicity

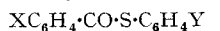
## D. Aryl phenacyl sulphides



Ref. No.	X	Y	% ' Total ' mortality		M.p., ° c	Formula	Analysis				Reference
							Found		Required		
			0.1%	0.025%			% C	% H	% C	% H	
2524	H	H	29	0	53-54	C <sub>14</sub> H <sub>12</sub> OS	—		—		12
2525	H	<i>p</i> -Cl	28	0	80-81	C <sub>14</sub> H <sub>11</sub> OCIS	—		—		13
2640	<i>p</i> -Cl	H	24	0	57-57.5	C <sub>14</sub> H <sub>11</sub> OCIS	63.9	3.8	64.0	4.2	*
2641	<i>p</i> -Cl	<i>p</i> -Cl	0	0	115-116	C <sub>14</sub> H <sub>10</sub> OCl <sub>2</sub> S	56.2	3.2	56.6	3.4	*
2643	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>	21	29	138-139	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> NCIS	54.5	2.9	54.6	3.3	*
							% N		% N		
2638	H	<i>p</i> -NO <sub>2</sub>	0	0	118	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> NS	—		—		14
2805	<i>p</i> -NO <sub>2</sub>	H	57	15	100-101	C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> NS	5.2		5.1		*
2644	<i>p</i> -NO <sub>2</sub>	<i>p</i> -Cl	11	8	104-105	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> NCIS	4.75		4.55		*

\* Prepared by R. F. B.

## E. Aryl thiolobenzoates



Ref. No.	X	Y	% ' Total ' mortality		M.p., ° c	Formula	Analysis				Reference
							Found		Required		
			0.1%	0.025%			% C	% H	% C	% H	
2442	H	H	23	—	55-56	C <sub>13</sub> H <sub>10</sub> OS	—	—	—	—	15
2441	H	<i>p</i> -Cl	97	36	74-75	C <sub>13</sub> H <sub>9</sub> OCIS	—	—	—	—	16
2445	<i>p</i> -Cl	H	64	8	81-82	C <sub>13</sub> H <sub>9</sub> OCIS	63.0	3.7	62.8	3.6	*
2440	<i>p</i> -Cl	<i>p</i> -Cl	P	0	134-135	C <sub>13</sub> H <sub>8</sub> OCl <sub>2</sub> S	55.2	2.9	55.0	2.8	*
							% N		% N		
2980	<i>p</i> -NO <sub>2</sub>	<i>p</i> -Cl	98	47	74-75	C <sub>13</sub> H <sub>8</sub> O <sub>3</sub> NCIS	4.8		4.8		*

\* Prepared by R. F. B.

P No assessment due to phytotoxicity

## F. Sulphides



Ref. No.	X	Y	% ' Total ' mortality		M.p., ° c or b.p., ° c/mm.	Formula	Analysis				Reference
							Found		Required		
			0.1 %	0.025 %			% C	% H	% C	% H	
2495	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	100	38	91-92	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub> S	—	—	—	—	17
2433	PhCH <sub>2</sub>	PhCH <sub>2</sub>	74	11	49-50	C <sub>14</sub> H <sub>14</sub> S	—	—	—	—	18
2432	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ·CH <sub>2</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ·CH <sub>2</sub>	98	32	40-42	C <sub>14</sub> H <sub>12</sub> Cl <sub>2</sub> S	—	—	—	—	5
2464	PhCH <sub>2</sub> ·CH <sub>2</sub>	PhCH <sub>2</sub> ·CH <sub>2</sub>	75	13	164-166/1.5	C <sub>16</sub> H <sub>18</sub> S	—	—	—	—	19
2416	Ph	PhCH <sub>2</sub> ·CH <sub>2</sub>	16	0	160-162/3.5	C <sub>14</sub> H <sub>14</sub> S	—	—	—	—	20
2469	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub> ·CH <sub>2</sub>	96	36	150-155/1.0	C <sub>14</sub> H <sub>13</sub> ClS	67.1	5.3	67.5	5.2	†
3151	Ph	PhCH:CH	P	26	150-151/1.5	C <sub>14</sub> H <sub>12</sub> S	78.5	5.2	79.2	5.7	**
3152	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	PhCH:CH	66	15	164-165/1.0	C <sub>14</sub> H <sub>11</sub> ClS	67.8	4.0	68.2	4.5	**
3191	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH:CH	P	13	99-100	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> S	59.4	3.3	59.8	3.55	**
2406	Ph	PhOCH <sub>2</sub> ·CH <sub>2</sub>	92	19	65-67	C <sub>14</sub> H <sub>14</sub> OS	73.4	6.3	73.0	6.1	†
3353	Ph	PhCH(OH)·CH <sub>2</sub>	30	10	168/2.0	C <sub>14</sub> H <sub>14</sub> OS	72.85	6.3	73.0	6.1	**

† Prepared by B. S. Jackson

\*\* Prepared by D. G.

P No assessment due to phytotoxicity

Table I (contd.)

G. Bis-sulphides											
X·S·R·S·X											
Ref. No.	X	R	% 'Total' mortality		M.p., °C	Formula	Analysis				Reference
			0.1%	0.025%			Found		Required		
							% C	% H	% C	% H	
2547	Ph	CCl:CCl	99	88	69-70	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> S <sub>2</sub>	—	—	—	21	
2956	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CCl:CCl	82	3	89-90	C <sub>14</sub> H <sub>8</sub> Cl <sub>4</sub> S <sub>2</sub>	44.2	2.1	44.0	2.1	**
3750	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> :CH(OH):CH <sub>2</sub>	17	3	45	C <sub>15</sub> H <sub>14</sub> OCl <sub>2</sub> S <sub>2</sub>	52.4	4.0	52.2	4.1	***
3751	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> :CHCl:CH <sub>2</sub>	15	6	85-86	C <sub>15</sub> H <sub>13</sub> Cl <sub>3</sub> S <sub>2</sub>	49.4	3.5	49.5	3.6	***
2221	PhCH <sub>2</sub>	CH:CH	88	28	60	C <sub>16</sub> H <sub>16</sub> S <sub>2</sub>	—	—	—	—	22
2362	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> :CH <sub>2</sub>	CH:CH	16	0	88	C <sub>16</sub> H <sub>14</sub> Cl <sub>2</sub> S <sub>2</sub>	56.2	4.0	56.3	4.1	†
2388	Ph	CH <sub>2</sub> :CH <sub>2</sub> :S:CH <sub>2</sub> :CH <sub>2</sub>	94	13	52	C <sub>16</sub> H <sub>18</sub> S <sub>3</sub>	—	—	—	—	23
2051	Ph	CO	30	—	41-42	C <sub>13</sub> H <sub>10</sub> OS <sub>2</sub>	—	—	—	—	24
2052	Ph	CS	6	—	96	C <sub>13</sub> H <sub>10</sub> S <sub>3</sub>	—	—	—	—	25
2957	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CMe <sub>2</sub>	100	3	54	C <sub>15</sub> H <sub>14</sub> Cl <sub>2</sub> S <sub>2</sub>	—	—	—	—	26
** Prepared by D. G.			*** Prepared by J. Fraser			† Prepared by B. S. Jackson					

\*\* Prepared by D. G.

\*\*\* Prepared by J. Fraser

† Prepared by B. S. Jackson

H. *N*-Benzyl-*N*-methylbenzenesulphenamides

XC <sub>6</sub> H <sub>4</sub> ·CH <sub>2</sub> ·N(CH <sub>3</sub> )·S·C <sub>6</sub> H <sub>4</sub> Y									
Ref. No.	X	Y	% ' Total ' mortality		M.p., ° c or b.p., ° c/mm.	Formula	Analysis		Refer- ence
			0.1 %	0.025 %			Found	Required	
							% N	% N	
2601	H	H	19	—	145-146/1.0	C <sub>14</sub> H <sub>15</sub> NS	5.8	6.1	*
2642	<i>p</i> -Cl	<i>p</i> -Cl	9	—	47.5-48	C <sub>14</sub> H <sub>13</sub> NCl <sub>2</sub> S	4.8	4.7	*
2602	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>	32	—	59.5-60.5	C <sub>14</sub> H <sub>13</sub> O <sub>2</sub> N <sub>2</sub> SCl	9.2	9.1	*
2740	<i>p</i> -NO <sub>2</sub>	H	19	—	49.5-50.5	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	10.0	10.2	*
2678	<i>p</i> -NO <sub>2</sub>	<i>p</i> -Cl	41	20	59.0-60.0	C <sub>14</sub> H <sub>13</sub> O <sub>2</sub> N <sub>2</sub> ClS	9.1	9.1	*
2600	<i>p</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>	17	—	96.5-97.5	C <sub>14</sub> H <sub>13</sub> O <sub>4</sub> N <sub>2</sub> S	13.2	13.2	*

\* Prepared by R. F. B.

Table II

The activity of various organic sulphides against eggs and young mites of red spider (further tests)

Test	Ref. No.	Substance	% 'Total' mortality at			
			0.05%	0.025%	0.0125%	0.00625%
I	2139	Dibenzyl disulphide	100	92	—	—
	2335	Bis- <i>p</i> -chlorobenzyl disulphide	100	52	—	—
II	2139	Dibenzyl disulphide	—	94	87	79
	2335	Bis- <i>p</i> -chlorobenzyl disulphide	—	71	36	7
III	2441	<i>p</i> -Chlorophenyl thiolobenzoate	54	9	—	—
	2388	Bis-2-phenylthioethyl sulphide	48	4	—	—
	2432	Bis- <i>p</i> -chlorobenzyl sulphide	31	12	—	—
	2433	Dibenzyl sulphide	26	6	—	—
IV	2462	Bis- <i>p</i> -fluorobenzyl disulphide	99	72	—	—
	2418	Bis-2-phenylethyl disulphide	95	85	59	—
	2476	Benzyl thiolobenzoate	97	71	48	17
	2477	Benzyl <i>p</i> -chlorothiobenzoate	99	79	72	60
	2485	<i>p</i> -Chlorobenzyl thiolobenzoate	100	94	78	—
V	2469	<i>p</i> -Chlorophenyl 2-phenylethyl sulphide	65	40	—	—
	2478	<i>p</i> -Chlorobenzyl <i>p</i> -chlorothiobenzoate	91	57	—	—
	2495	Bis- <i>p</i> -chlorophenyl sulphide	70	21	—	—
VI	2675	Benzyl <i>p</i> -nitrothiolobenzoate	100	100	76	48
	2547	1 : 2-Dichloro-1 : 2-bisphenylthioethylene	84	82	53	37
	2957	2 : 2-Bis- <i>p</i> -chlorophenylthiopropene	62	32	18	6
VII	2547	1 : 2-Dichloro-1 : 2-bisphenylthioethylene	92	76	48	28

The benzyl thiolobenzoates (—CO·S·CH<sub>2</sub>—) were generally more active than the isomeric aryl phenylthioacetates (—S·CO·CH<sub>2</sub>—) and the corresponding phenyl thiolobenzoates (—CO·S—). The aryl phenacyl sulphides (—S·CH<sub>2</sub>·CO—) were least active.

In comparing the activity of compounds substituted by chlorine in the *para* position of the

nucleus against the corresponding unsubstituted compounds there was no general rule. Sometimes the unsubstituted compounds were the most active, e.g. dibenzyl disulphide (Ref. No. 2139), 1 : 2-dichloro-1 : 2-bisphenylthioethylene (Ref. No. 2547) and 1 : 2-bisbenzylthioethylene (Ref. No. 2221) were more active than the corresponding nuclear substituted compounds (Ref. Nos. 2335, 2956 and 2362). In other cases, however, the unsubstituted compounds were either inactive or much less active than the *para*-chlorine-substituted compounds. Thus, phenyl phenylthioacetate (Ref. No. 2523) and phenyl 2-phenylethyl sulphide (Ref. No. 2416) were less active than the corresponding substituted compounds (Ref. Nos. 2534, 2639, 2679 and 2469). In other active groups—e.g. the benzyl thiolobenzoates and the dibenzyl sulphides—the substituted and the unsubstituted compounds had the same order of activity.

Similar variation is found on comparing the effect on activity of bis-*para*-chlorination against mono-*para*-chlorination. In the phenyl phenylthioacetates, the bis-*para*-chlorinated derivative (Ref. No. 2679) was the most active compound but in the phenyl thiolobenzoates the bis-*para*-chlorinated derivative (Ref. No. 2440) was probably less active than either of the mono-*para*-chlorinated compounds (Ref. Nos. 2441 and 2445). In the benzyl thiolobenzoates the bis- (Ref. No. 2478) and mono-*para*-chlorinated derivatives had a very similar order of activity.

Eaton & Davies<sup>27</sup> found that, in a series of compounds containing two benzene nuclei connected by certain bridging groups, activity to the summer eggs and adults of fruit tree red spider (*M. ulmi* Koch) could be influenced by substitution in the benzene nuclei. Maximum activity appeared to be associated with chlorine substitution in the *para* position in one nucleus and also with compounds of this type having unsubstituted nuclei. Kenaga<sup>28</sup> found with a series of substituted phenyl benzoates, and Kenaga & Hummer<sup>29</sup> with a series of substituted phenyl benzenesulphonates, that maximum ovicidal activity (two-spotted spider mite) occurred where both benzene nuclei were substituted with chlorine in the *para* position.

The present findings show that no general conclusions of this type can be applied to different groups of organic compounds containing two benzene nuclei connected by a bridging group, although they confirm that *para*-chlorination often has a marked effect and may yield more active compounds.

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