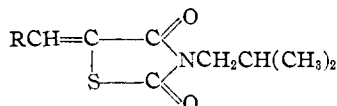


TABLE I



R	Yield, %	M.p., °C.	Formula	Kjeldahl Nitrogen, %		Sulfur, %	
				Calcd.	Found	Calcd.	Found
C <sub>6</sub> H <sub>5</sub>	67	113-116	C <sub>14</sub> N <sub>15</sub> NO <sub>2</sub> S	5.4	5.1	12.3	12.6
C <sub>6</sub> H <sub>5</sub> CH=CH-	24	128-130	C <sub>18</sub> H <sub>17</sub> NO <sub>2</sub> S	4.9	4.8	11.1	11.3
4-Cl-C <sub>6</sub> H <sub>4</sub> -	33	145-147	C <sub>14</sub> H <sub>14</sub> ClNO <sub>2</sub> S	4.8	4.4	" <sup>a</sup>	" <sup>a</sup>
3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -	62	116-118	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> S	9.2	9.2 <sup>b</sup>	..	..
4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	40	106-108	C <sub>15</sub> H <sub>17</sub> NO <sub>3</sub> S	4.8	4.8	11.0	11.4
3,4-(OCH <sub>2</sub> O)C <sub>6</sub> H <sub>3</sub> -	55	122-124	C <sub>15</sub> H <sub>15</sub> NO <sub>3</sub> S	4.6	4.3	10.5	10.8

<sup>a</sup> Calcd.: Cl, 12.0. Found: Cl, 11.8. <sup>b</sup> By A.O.A.C. salicylic acid + sodium thiosulfate method.

pyrethrum. The 5-piperonylidene-3-isobutyl-2,4-thiazolidinedione is of particular interest because many of the commercial synergists for pyrethrum such as piperonyl butoxide,<sup>12</sup> piperonylcyclonene,<sup>12</sup> sesamin,<sup>13</sup> propyl isome<sup>14</sup> and others, contain the methylenedioxyphenyl group. It is to be pointed out that although many compounds containing such a group are insecticidally active, the presence of a methylenedioxyphenyl group in the structure of a compound is not a sufficient condition for insecticidal activity or for synergistic activity with pyrethrum.<sup>15</sup>

The condensation of aromatic aldehydes with 2,4-thiazolidinedione gave 5-aralkylidene-2,4-thiazolidinediones in good yields. The latter compounds formed potassium salts which were readily isolated. The reaction of these potassium salts with isobutyl bromide was carried out in dimethylformamide as recommended by Sheehan and Bolhofer<sup>16</sup> for the alkylation of phthalimide.

All of the six 5-aralkylidene-3-isobutyl-2,4-thiazolidinediones thus prepared are crystalline solids which have rather low solubility in organic solvents. As a matter of fact, the benzylidene and the piperonylidene compounds are so insoluble that no testing was contemplated. The other four compounds were evaluated as fly toxicants, alone and in combination with pyrethrin. They were found to have insufficient activity to be of interest.

#### Experimental<sup>17</sup>

The 5-aralkylidene-2,4-thiazolidinediones were prepared by the condensation of aromatic aldehydes with 2,4-thiazolidinedione in acetic acid containing anhydrous sodium acetate.<sup>18</sup>

5-(*p*-Chlorobenzylidene)-2,4-thiazolidinedione, m.p. 223-225°, yield 75%. *Anal.* Calcd. for C<sub>10</sub>H<sub>6</sub>ClNO<sub>2</sub>S: N, 5.9. Found: N, 5.6.

5-Anisylidene-2,4-thiazolidinedione, m.p. 212-214°, yield 84%. *Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>NO<sub>2</sub>S: N, 6.0. Found: N, 5.9.

(12) H. Wachs, *Science*, **105**, 530 (1947).

(13) (a) C. Eagelson, U. S. Patent, 2,202,145 (1940); (b) H. L. Haller, E. R. McGovran, L. D. Goodhue and W. N. Sullivan, *J. Org. Chem.*, **7**, 183 (1942); (c) E. A. Parkin and A. A. Green, *Nature*, **153**, 594 (1944).

(14) M. E. Synerholm and A. Hartzell, *Contrib. Boyce Thompson Inst.*, **14**, 79 (1945).

(15) See, for example, E. A. Prill and M. E. Synerholm, *ibid.*, **14**, 221 (1946). For a discussion of the effect of the methylenedioxyphenyl group on the synergistic action of amides, see ref. 8.

(16) J. C. Sheehan and W. A. Bolhofer, *THIS JOURNAL*, **72**, 2787 (1950).

(17) All melting points are uncorrected.

(18) (a) F. Kucera, *Monatsh.*, **35**, 137 (1914); (b) D. Libermann, J. Himbert and L. Hengl, *Bull. soc. chim. France*, 1120 (1948).

#### Potassium Salts of 5-Aralkylidene-2,4-thiazolidinediones.

—A mixture of 5-aralkylidene-2,4-thiazolidinedione (0.25 mole), potassium hydroxide (15.4 g., 0.275 mole) and ethanol (500 ml.) was stirred and warmed on a steam-bath for three hours. After cooling, the potassium salt was collected and dried in an oven. The yields of the potassium salts were usually over 90%. They were used in the following alkylations without further purification.

5-Aralkylidene-3-isobutyl-2,4-thiazolidinediones.—The above potassium salt of a 5-aralkylidene-2,4-thiazolidinedione (0.2 mole) was heated under reflux with isobutyl bromide (34 g., 0.25 mole) in dimethylformamide (350 ml.) for three hours. After cooling to room temperature, the reaction mixture was poured into water. The precipitate of 5-aralkylidene-3-isobutyl-2,4-thiazolidinedione was collected and recrystallized from ethylene dichloride or a mixture of methanol and acetone.

The six 5-aralkylidene-3-isobutyl-2,4-thiazolidinediones prepared, their yields, physical properties and analytical data are given in Table I.

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#### The Reaction of 1-Hexyne and Diethyl Fumarate

BY M. J. HOGSED AND R. V. LINDSEY

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Although conjugated systems containing triple bonds undergo the Diels-Alder reaction,<sup>1</sup> the pseudo-Diels-Alder reaction of monoolefins and dienophiles to yield δ,ε-unsaturated adducts<sup>2</sup> had not been extended to monoacetylenes and dienophiles. Accordingly, an investigation of the reaction of 1-hexyne with diethyl fumarate was undertaken.

When these reactants were heated in an autoclave at 230° for 4 hr., two products were isolated. The major component corresponded to the reaction product of two moles of diethyl fumarate with one mole of 1-hexyne and has not been further characterized although a probable structure is suggested from consideration of the reaction mechanism. The minor product, and probable precursor of the diadduct as discussed below, was a monoadduct containing allenic unsaturation as indicated by infrared data. This product on hydrogenation and subsequent saponification gave a saturated dibasic

(1) L. W. Butz, A. M. Gaddis, E. W. J. Butz and R. E. Davis, *J. Org. Chem.*, **6**, 379 (1940).

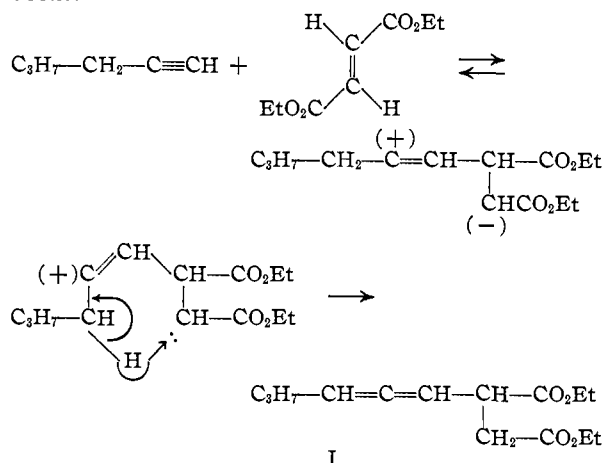
(2) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943).

acid identified as *n*-hexylsuccinic acid. The monoadduct appears to have structure I.

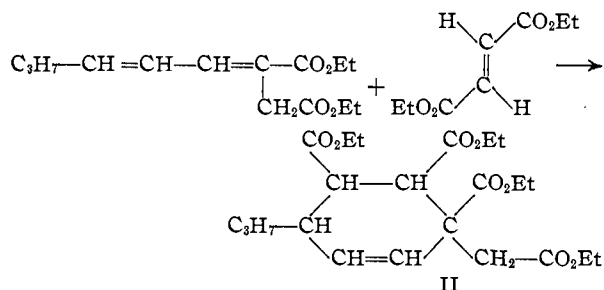
### Discussion

Arnold and Dowdell<sup>3</sup> have proposed that the reaction of monoolefins with dienophiles proceeds *via* a transient cyclic complex. The possibility of a short-lived ionic intermediate was not excluded. It also has been proposed<sup>1</sup> that when vinyl acetylenes react with dienophiles, the first product may be an allenic adduct. A combination of these two proposals satisfactorily explains our experimental results.

In the reaction of 1-hexyne and diethyl fumarate, a short-lived ionic intermediate appears to be necessary. Since the system C—C≡C is linear, addition and hydrogen transfer cannot be simultaneous; however, the formation of an ionic intermediate would allow the alkyl group to swing into position and the hydrogen transfer could then occur.



A probable mode of formation of the major product, the diadduct, then becomes apparent. Under the conditions of the reaction, rearrangement of the allene to a diene is likely,<sup>4</sup> especially since an  $\alpha,\beta,\gamma,\delta$ -di-unsaturated ester would be formed. The resulting diene could react with another molecule of diethyl fumarate to yield the diadduct II.



### Experimental Details

**Reaction of 1-Hexyne and Diethyl Fumarate.**—A mixture of 30 g. of 1-hexyne (Farchan Research Labs.) and 200 g. of diethyl fumarate was heated in a stainless steel autoclave at

(3) R. T. Arnold and J. F. Dowdell, *THIS JOURNAL*, **70**, 2590 (1948).

(4) B. K. Mereshkowski, *J. Russ. Phys. Chem. Soc.*, **45**, 1940 (1913); G. Egloff, G. Hulla and V. I. Komarevsky, "Isomerization of Pure Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1942, p. 73.

230° for 4 hr. On distillation, 10.5 g. of 1-hexyne and 116 g. of diethyl fumarate were recovered. The minor product, 4 g., b.p. 140–150° (6 mm.), and the major product, 50.5 g., b.p. 195–199° (1 mm.),  $n_D^{25}$  1.4641, were isolated by distillation. The major product was found by analysis to correspond to a 2:1 diethyl fumarate/1-hexyne adduct.

*Anal.* Calcd. for C<sub>22</sub>H<sub>34</sub>O<sub>6</sub>: C, 62.0; H, 8.0. Found: C, 61.9; H, 8.2.

Infrared absorption at 6.0 and 10.3  $\mu$  indicated internal unsaturation; the spectrogram showed no allenic band at 5.1  $\mu$ . No further characterization of this adduct was undertaken.

**Structure of the Monoadduct.**—The infrared absorption spectrogram of this adduct showed a strong band at 5.1  $\mu$  characteristic of alkenes.<sup>5</sup> For identification, the adduct was hydrogenated in methanol at 2–3 atmospheres hydrogen pressure with a 10% palladium-on-charcoal catalyst, and the hydrogenated product was saponified with alcoholic potassium hydroxide by standard procedures. The acid obtained was identified as *n*-hexylsuccinic acid by conversion to *n*-hexylsuccinamic acid, m.p. 119–121° (lit.<sup>6</sup> 122°). The melting point was undepressed on admixture with the anilic acid prepared from an authentic sample of *n*-hexylsuccinic acid made essentially by the method of Alder, Söll and Söll.<sup>7</sup>

As a further check, the unknown acid was converted to its *p*-toluidide, m.p. 78–80°. The melting point was unchanged on mixing with a sample of *N-p*-tolyl-*n*-hexylsuccinimide prepared from the authentic sample of *n*-hexylsuccinic acid.

*Anal.* Calcd. for C<sub>17</sub>H<sub>23</sub>O<sub>2</sub>N: C, 74.7; H, 8.5; N, 5.1. Found: C, 74.1; H, 8.4; N, 5.2.

(5) J. H. Wotiz and W. D. Celmer, *THIS JOURNAL*, **74**, 1860 (1952); R. B. Barnes, R. C. Gore and R. W. Stafford, *Anal. Chem.*, **20**, 402 (1948).

(6) A. Higson and J. F. Thorpe, *J. Chem. Soc.*, **89**, 1471 (1906).

(7) K. Alder, H. Söll and H. Söll, *Ann.*, **565**, 75 (1949).

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### The Indicator and Dye Properties of Some Aromatic Phosphonic Acids and their Arsenic Analogs

BY GENNADY M. KOSOLAPOFF AND GERALD G. PRIEST

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It is not uncommon to find in reviews and treatises dealing with dyestuffs a mention of the possibilities of the utilization of acidic groups other than the commonly employed sulfonic acids in synthesis of materials that have dyeing properties. Yet, one is unable to find concrete information about the fundamental properties of such dye analogs in the chemical literature. It was in order to supply such data that the present study was made. The model substances selected for analog variations were methyl orange, ethyl orange and congo red. This choice, for the present investigation, was made for two reasons. The synthesis of analogs of these dyes containing either the phosphonic or the arsenic acid residues can be accomplished quite readily from easily obtainable intermediates. At the same time, the relatively small molecules of these analogs should be expected to display any property differences more readily than more complex dye molecules. Finally, since the sulfonate model compounds are rather well known indicators, the present choice of the analogs permits, as well, a comparison of the indicator properties of these substances.

Generally, the dyeing properties of the compounds under present consideration can be summa-