luted with water and the resulting solid filtered. This solid was recrystallized from acetone–water, giving 1.3 g. of yellow solid, melting over the range 185–203° (96% crude yield). A second recrystallization from this solvent did not improve the m.p. Recrystallization from a large amount of petroleum ether (b.p. 77–115°) gave 1 g. (74%) of yellow needles melting at 210–212°.

Anal. Calcd. for $C_{12}H_6O_3NBr$: Br, 27.38. Found: Br, 27.35, 27.30.

4-Aminodibenzofuran.—A procedure for the preparation of 2-aminodibenzofuran *via* metalation and reaction with O-methylhydroxylamine appears in the Doctoral Dissertation of Willis,[9] but has not been published elsewhere. The following is a modification of that procedure.

To a solution of 42 g. (0.25 mole) of dibenzofuran in 150 ml. of anhydrous ether was added 0.4 mole of *n*-butyllithium.[10] The solution was stirred at room temperature for 38 hours; at the end of this period, Color Test II[11] remained positive. To this solution (cooled in an ice–salt-bath) was added slowly 6.1 g. (0.13 mole) of O-methylhydroxylamine in 40 ml. of ether. The free amine was prepared from O-methylhydroxylamine hydrochloride[12] by treatment with 50% sodium hydroxide, the resulting vapors being passed over some pellets of potassium hydroxide in a heated U-tube and subsequently condensed. Soon after the addition of the base, Color Test I[13] became negative. The solution was stirred an additional 2 hours and then hydrolyzed slowly with ice water. The ethereal layer was separated and the aqueous solution extracted twice with ether. The combined extracts were dried over sodium sulfate and the ethereal solution subsequently treated with dry hydrogen chloride to precipitate the amine hydrochloride. The 4-aminodibenzofuran hydrochloride was dissolved in 1 liter of water and the solution made alkaline. The tan colored amine was collected by filtration; the yield was 12.9 g. (54%, based on the O-methylhydroxylamine or 79%, based on the amount of dibenzofuran used), melting at 83–84°.

3-Nitrodibenzofuran from 3-Aminodibenzofuran.—Thirteen milliliters of concentrated hydrochloric acid, 8 ml. of water and 9.2 g. (0.05 mole) of 3-aminodibenzofuran were placed in the reaction flask and cooled in a salt–ice-bath. To this mixture was slowly added 4 g. of sodium nitrite in 10 ml. of water. The solution was then carefully neutralized with calcium carbonate and filtered. Into the filtrate was stirred 8.0 g. of finely powdered sodium cobaltinitrite, and the resulting crystalline diazonium salt was filtered. The diazonium cobaltinitrite (still wet) was added portionwise, at room temperature, to a well stirred solution of 5 g. of sodium nitrite and 5 g. of cupric sulfate in 40 ml. of water in which 3 g. of cupric oxide was suspended. This mixture was stirred overnight and filtered. The residue was refluxed with portions of glacial acetic acid and filtered. The combined filtrates were concentrated to about 100 ml. and cooled to allow crystallization of the 3-nitrodibenzofuran. There was thus obtained 7.6 g. (71%) of crude product melting from 140–152°. Two recrystallizations from glacial acetic acid brought the m.p. range to 165–179°. An additional recrystallization from absolute ethanol and finally again from glacial acetic acid brought the m.p. to 181–182°; the final yield was 3.3 g. (31%). A mixed m.p. with authentic 3-nitrodibenzofuran was not depressed.

4-Nitrodibenzofuran from 4-Aminodibenzofuran.—Into the reaction flask were placed 9 ml. of hydrochloric acid, 5 ml. of water and 6.1 g. (0.0333 mole) of 4-aminodibenzofuran; this mixture was cooled in a salt–ice-bath. Sodium nitrite (2.5 g.) in 10 ml. of water was added slowly. The diazonium cobaltinitrite was prepared and decomposed as above. Recrystallization from dilute ethanol gave a yellow solid, melting from 60–90°; further recrystallization from this solvent did not improve the m.p. One recrystallization from petroleum ether (b.p. 77–115°) raised the m.p. range to 132–136°. Two additional recrystallizations gave tan needles melting at 138–139°; the same m.p. for 4-nitrodibenzofuran is reported by Yamashiro.[14] The final yield was 1.5 g. (21%); in a second run, eliminating the ethanolic recrystallization, a 28% yield was obtained.

Department of Chemistry
Iowa State College
Ames, Iowa

---

[9] H. B. Willis, Doctoral Dissertation, Iowa State College, 1943.

[10] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949).

[11] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

[12] Eastman Kodak Company, White Label.

[13] H. Gilman and F. Schulze, This Journal, **47**, 2002 (1925).

[14] S. Yamashiro, *J. Chem. Soc. Japan*, **59**, 945 (1938) [*C. A.*, **33**, 603 (1939)].

5-Aralkylidene-3-isobutyl-2,4-thiazolidinediones

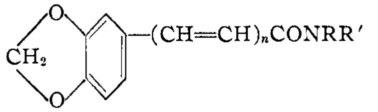
By Chien-Pen Lo, Elwood Y. Shropshire and W. J. Croxall

Received March 14, 1953

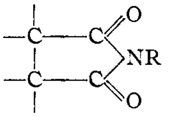
A number of isobutyramides of unsaturated acids, *e.g.*, affinin (I),[1,2] herculin (II),[3,5] pellitorine (III)[4,5] and scabrin (IV),[6] have been isolated from various plants and shown to have insecticidal properties comparable to pyrethrins. Many fagaramides (V)[7] and piperamides (VI)[8,9] are known to have synergistic activity with pyrethrum. All these are derivatives of acrylamide. It is also known that some N-alkyl cyclic imides of the general structure VII[10] are synergists for pyrethrins. The present paper reports the synthesis of a few 5-aralkylidene-3-isobutyl-2,4-thiazolidinediones (VIII) which contain both the acrylamide and the cyclic imide structures for testing as fly toxicants. These compounds were prepared by the isobutylation of 5-aralkylidene-2,4-thiazolidinediones. The choice of the isobutyl group is based on the fact that all the aforementioned naturally occurring unsaturated acid amides are isobutylamides and that N-isobutylundecylenamide[11] is a synergist for

$R—CH=CHCONHCH_2CH(CH_3)_2$

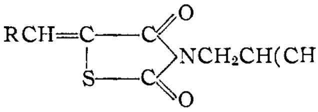
I, $R = CH_3(CH=CH)_2(CH_2)_2–$
II, $R = CH_3(CH_2)_2CH=CH(CH_2)_4–$
III, $R = CH_3(CH_2)_2CH=CH(CH_2)_2–$
IV, $R = C_{15}H_{23}–$



V, $n = 1$
VI, $n = 2$



VII



VIII

---

[1] (a) F. Acree, M. Jacobson and H. L. Haller, *J. Org. Chem.*, **10**, 237 (1945); (b) F. Acree. M. Jacobson and H. L. Haller. *ibid.*, **10**, 449 (1945); (c) M. Jacobson, F. Acree and H. L. Haller, *ibid.*, **12**, 731 (1947).

[2] For simplicity, the name affinin is used here despite the fact that the original authors proposed to discontinue the use of this name (ref. 1c).

[3] M. Jacobson, This Journal, **70**, 4234 (1948).

[4] M. Jacobson, *ibid.*, **71**, 366 (1949).

[5] There is now some doubt as to the correctness of the gross structures originally assigned to natural herculin and pellitorine. See L. Crombie, *J. Chem. Soc.*, 2997, 4338 (1952); *Chem. and Ind.*, 1034 (1952). We are grateful to the referee for this information.

[6] M. Jacobson, This Journal, **73**, 100 (1951).

[7] S. I. Gertler and H. L. Haller, U. S. Patent 2,326,350 (1943).

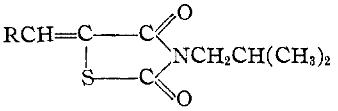
[8] E. K. Harvill, A. Hartzell and J. M. Arthur, *Contrib. Boyce Thompson Inst.*, **13**, 87 (1944).

[9] Piperine, the piperidide of piperic acid, (VI, $RR' = –(CH_2)_5–$) is highly toxic to houseflies either used alone or in combination with pyrethrum (ref. 8).

[10] (a) H. W. Arnold and N. E. Searle, U. S. Patent 2,462,835 (1949); (b) A. A. Schreiber, U. S. Patent 2,476,512 (1949).

[11] (a) A. Weed, *Soap*, **14**, 133 (1938); (b) E. W. Bousquet, U. S. Patent 2,166,119–20 (1939); (c) W. A. L. Davis and P. Bracey, *Nature*, **153**, 594 (1944).

TABLE I



R	Yield, %	M.p., °C.	Formula	Kjeldahl Nitrogen, % Calcd.	Kjeldahl Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
C_6H_5	67	113–116	$C_{14}N_{15}NO_2S$	5.4	5.1	12.3	12.6
$C_6H_5CH{=}CH$–	24	128–130	$C_{16}H_{17}NO_2S$	4.9	4.8	11.1	11.3
4-Cl–C_6H_4–	33	145–147	$C_{14}H_{14}ClNO_2S$	4.8	4.4	..[a]	..[a]
3-NO_2–C_6H_4–	62	116–118	$C_{14}H_{14}N_2O_4S$	9.2	9.2[b]	..	..
4-CH_3O–C_6H_4–	40	106–108	$C_{15}H_{17}NO_3S$	4.8	4.8	11.0	11.4
3,4-(OCH_2O)C_6H_3–	55	122–124	$C_{15}H_{15}NO_4S$	4.6	4.3	10.5	10.8

[a] Calcd.: Cl, 12.0. Found: Cl, 11.8. [b] 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,[12] piperonylcyclonene,[12] sesamin,[13] propyl isome[14] 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.[15]

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[16] 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[17]

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.[18]

5-(*p*-Chlorobenzylidene)-2,4-thiazolidinedione, m.p. 223–225°, yield 75%. *Anal.* Calcd. for $C_{10}H_6ClNO_2S$: N, 5.9. Found: N, 5.6.

5-Anisylidene-2,4-thiazolidinedione, m.p. 212–214°, yield 84%. *Anal.* Calcd. for $C_{11}H_9NO_3S$: N, 6.0. Found: N, 5.9.

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-thiazolidenediones prepared, their yields, physical properties and analytical data are given in Table I.

Acknowledgment.—The authors are indebted to Dr. F. B. Maughan and his associates for the insecticidal evaluations and to Mr. T. P. Callan and his staff for chemical analyses.

ROHM AND HAAS COMPANY
PHILADELPHIA 37, PENNSYLVANIA

---

[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).

The Reaction of 1-Hexyne and Diethyl Fumarate

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

RECEIVED MAY 13, 1953

Although conjugated systems containing triple bonds undergo the Diels–Alder reaction,[1] the pseudo-Diels–Alder reaction of monoölefins and dienophiles to yield δ,ϵ-unsaturated adducts[2] 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.*, **5**, 379 (1940).

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