thermocouple, B and S gauge 20, inserted through the side arm to 1/4 in. from the receiving coil. This assembly has been operated from $-60°$ to 120° C with resolution equal to that obtained in instruments without a thermostated assembly. Figure 3 shows a trace obtained for the aldehydic proton of acetaldehyde. The resolution is at least one part in 10^8. Since the receiver coil may be tuned without disassembling the apparatus, it is used for routine investigations as well as variable temperature studies.

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SOME HYPOGLYCEMIC THIADIAZOLES

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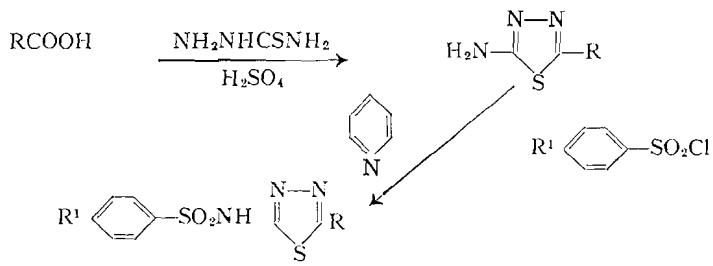
In 1942 Janbon (1) first noticed that 2-sulphanilamido-5-isopropyl-1,3,4-thiadiazole caused hypoglycemia. Bovet and Dubost (2) as well as Loubatières (3) studied the relationship between structure and activity in this series. The present work was undertaken in an effort to prepare some new hypoglycemic thiadiazoles.

A series of 2-arylsulphonamido-5-alkyl-1,3,4-thiadiazoles (Table II) was synthesized according to the following reaction scheme.



The pharmacology of these compounds will be reported elsewhere.

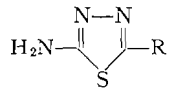
EXPERIMENTAL

2-Amino-5-alkyl-1,3,4-thiadiazoles (*Table I*)

A well-stirred mixture of 0.3 mole of fatty acid, 31.5 ml of concentrated sulphuric acid, and 0.25 mole of thiosemicarbazide was slowly heated to 80–90° and maintained at that temperature for 7 hours. After the reaction mixture was cooled, it was poured into ice water and made basic with concentrated ammonia. The crude product, which precipitated upon addition of the ammonia, was filtered and washed with water. It was recrystallized from alcohol–water.

TABLE I

2-Amino-5-alkyl-1,3,4-thiadiazoles



R	M.p., ° C	Yield, %	Formula	Analysis, % Calculated C	Calculated H	Found C	Found H
n-C_3H_7	203–206	80	$C_5H_9N_3S$	*a*			
iso-C_3H_7	182–185	70	$C_5H_9N_3S$	*b*			
n-C_4H_9	194–196	35	$C_6H_{11}N_3S$	*b*			
iso-C_4H_9	228–230	49	$C_6H_{11}N_3S$	*b*			
t-C_4H_9	181–184	54	$C_6H_{11}N_3S$	45.80	7.03	45.84	7.04
sec-C_4H_9	178–180	55	$C_6H_{11}N_3S$	45.80	7.03	45.71	6.82
n-C_5H_{11}	194–196	52	$C_7H_{13}N_3S$	*c*			
iso-C_5H_{11}	214–215	52	$C_7H_{13}N_3S$	49.09	7.59	48.71	7.63

[a]Ohta, M. and Higashijima, T. J. Pharm. Soc. Japan, **72**, 376 (1952).
[b]Wojan, H. and Wuckel, H. Arch. Pharm. **284**, 53 (1951).
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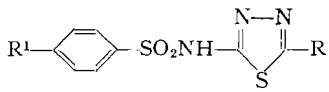
TABLE II

2-Arylsulphonamido-5-alkyl-1,3,4-thiadiazoles



R	R^1	M.p., ° C	Yield, %	Formula	Analysis, % Calculated C	Calculated H	Found C	Found H
n-C_3H_7	CH_3	134–136	59	$C_{12}H_{15}O_2N_3S_2$	48.45	5.08	48.62	5.08
n-C_3H_7	OCH_3	125–127	65	$C_{12}H_{15}O_3N_3S_2$	45.98	4.82	46.01	4.81
n-C_3H_7	OC_2H_5	122–124	62	$C_{13}H_{17}O_3N_3S_2$	47.69	5.24	47.69	5.84
iso-C_3H_7	CH_3	119–121[a]	60	$C_{12}H_{15}O_2N_3S_2$	48.45	5.08	48.36	5.12
iso-C_3H_7	OCH_3	141–142[a]	57	$C_{12}H_{15}O_3N_3S_2$	45.98	4.82	45.96	4.64
iso-C_3H_7	OC_2H_5	128–130	65	$C_{13}H_{17}O_3N_3S_2$	47.69	5.24	47.88	5.53
n-C_4H_9	CH_3	115–116	69	$C_{13}H_{17}O_2N_3S_2$	50.13	5.50	49.89	5.75
n-C_4H_9	OCH_3	121–123	74	$C_{13}H_{17}O_3N_3S_2$	47.69	5.24	47.89	4.98
n-C_4H_9	OC_2H_5	112–113	54	$C_{14}H_{19}O_3N_3S_2$	49.25	5.61	49.49	5.74
iso-C_4H_9	CH_3	174–175	50	$C_{13}H_{17}O_2N_3S_2$	50.13	5.50	49.97	5.61
iso-C_4H_9	OCH_3	148–149	68	$C_{13}H_{17}O_3N_3S_2$	47.69	5.24	47.53	4.75
iso-C_4H_9	OC_2H_5	151–152	67	$C_{14}H_{19}O_3N_3S_2$	49.25	5.61	48.81	5.78
iso-C_4H_9	Cl	154–155	44	$C_{12}H_{14}O_2N_3S_2Cl$	43.40	4.25	43.85	4.45
t-C_4H_9	CH_3	148–150	64	$C_{13}H_{17}O_2N_3S_2$	50.13	5.50	49.95	5.68
t-C_4H_9	OCH_3	140–141	74	$C_{13}H_{17}O_3N_3S_2$	47.69	5.24	47.70	5.09
t-C_4H_9	OC_2H_5	161–162	52	$C_{14}H_{19}O_3N_3S_2$	49.25	5.61	49.22	5.52
t-C_4H_9	Cl	163–165	45	$C_{12}H_{14}O_2N_3S_2Cl$	43.40	4.25	43.30	4.48
sec-C_4H_9	CH_3	111–112	40	$C_{13}H_{17}O_2N_3S_2$	50.13	5.50	49.64	5.67
sec-C_4H_9	OCH_3	97–98	40	$C_{13}H_{17}O_3N_3S_2$	47.69	5.24	47.45	4.74
sec-C_4H_9	OC_2H_9	106–107	50	$C_{14}H_{19}O_3N_3S_2$	49.25	5.61	48.80	5.89
n-C_5H_{11}	CH_3	131–132	73	$C_{14}H_{19}O_2N_3S_2$	51.64	5.89	51.64	5.68
n-C_5H_{11}	OCH_3	133–134	65	$C_{14}H_{19}O_3N_3S_2$	49.25	5.61	48.83	5.64
n-C_5H_{11}	OC_2H_5	116–117	57	$C_{15}H_{21}O_3N_3S_2$	50.69	5.96	50.77	5.77
iso-C_5H_{11}	CH_3	140–141	73	$C_{14}H_{19}O_2N_3S_2$	51.64	5.89	51.86	5.72
iso-C_5H_{11}	OCH_3	141–142	65	$C_{14}H_{19}O_3N_3S_2$	49.25	5.61	48.91	5.78
iso-C_5H_{11}	OC_2H_5	99–100	57	$C_{15}H_{21}O_3N_3S_2$	50.69	5.96	50.62	5.89

[a]Ruschig, H., Korger, G., Aumuller, W., Wagner, H., and Weyer, R. Arzneimittel-Forsch. **8**, 448 (1958), have reported melting points for these compounds.

2-Arylsulphonamido-5-alkyl-1,3,4-thiadiazoles (*4*) (*Table II*)

A solution of 0.06 mole of the arylsulphonyl chloride in 25 ml pyridine was slowly added with stirring to a solution of 0.06 mole of 2-amino-5-alkyl-1,3,4-thiadiazole in 25 ml pyridine. The resulting solution, after being allowed to stand overnight at room temperature, was slowly added to an excess of 6 *N* hydrochloric acid. The crude product separated, usually as a solid but sometimes as a yellow gum which crystallized on standing. It was dissolved in dilute sodium hydroxide, treated with charcoal, and reprecipitated with hydrochloric acid. The 2-arylsulphonamido-5-alkyl-1,3,4-thiadiazole was recrystallized from alcohol–water.

Microanalyses were performed by Dr. Carl Tiedcke, Teaneck, N.J., U.S.A.

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NOTE ON THE PHOTOOXIDATION OF TETRAMETHYLRUBRENE*

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Badger's group (1) first noticed that tetramethylrubrene (5,6,11,12-tetra-*p*-tolylnaphthacene) crystals change from their normal deep red to a colorless form on exposure to sunlight. This is not a widely observable phenomenon in as much as substances which are photochemically active when dissolved in a suitable solvent do not normally undergo the same reaction in the pure crystalline form. Rubrene (5,6,11,12-tetraphenylnaphthacene) was found to exhibit the same type of decoloration on exposure to ultraviolet irradiation (3), but in this case specially prepared thin films on a large area substrate were necessary. In each case the product is a transannular peroxide.

It is the purpose of this note to report the results of some experiments on the photooxidation of tetramethylrubrene crystals. The experiments were done at 25° C in cells with plane quartz windows. The light source was a 1-kw AH6 water-cooled mercury arc. The apparatus was as previously described by Hochstrasser and Ritchie (3), and differential pressure measurements could be made to within 0.002 mm Hg at total pressures below 25 mm Hg. The oxidation was followed by noting the changes of oxygen pressure in a constant volume system as the crystals were illuminated with near monochromatic light. The small crystals were scratched on to the surface of a quartz disk (in the absence of absorbable light) and the disk was then carefully sealed on to one end of a cylindrical cell. The cell was then evacuated, oxygen allowed in to a known pressure in the dark, and when stability was maintained the crystals were illuminated and the decrease in pressure determined as a function of time. Experiments involving intermittent illumination and irradiation with light at two wavelengths were performed.

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