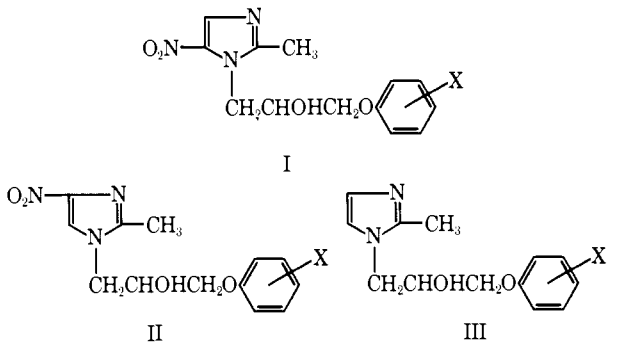
TABLE I

No.	Group	X	Mp, °C	Yield,[a] %	Recrystn solvent[b]	Formula[c]	Analgetic act.[f]	Antitrichomonal *in vitro* act.: g/ml × 10^{-3} [g]
1	I	H	132–133	44.5	A	$C_{13}H_{15}N_3O_4$		1:250
2		*o*-CH_3	141–142	36.2	B	$C_{14}H_{17}N_3O_4$		1:300
3		*m*-CH_3	105–106	38.0	A	$C_{14}H_{17}N_3O_4$		
4		*p*-CH_3	104–105	31.0	A	$C_{11}H_{17}N_3O_4$		
5		*o*-Cl	137–138	29.0	B	$C_{13}H_{14}ClN_3O_4$		1:300
6		*p*-Cl	157–158	23.0	B	$C_{13}H_{14}ClN_3O_4$		
7		*o*-OCH_3	114–115	41.0	A	$C_{14}H_{17}N_3O_5$		1:80
8		*p*-OCH_3	107.5–108.5	43.0	A	$C_{14}H_{17}N_3O_5$		
9	II	H	161–162	56.8	A	$C_{13}H_{15}N_3O_4$	+	
10		*o*-CH_3	167–168.5	58.0	A	$C_{14}H_{17}N_3O_4$[d]	+	
11		*m*-CH_3	159–160	46.0	A	$C_{14}H_{17}N_3O_4$[e]		
12		*p*-CH_3	158–159	44.2	A	$C_{14}H_{17}N_3O_4$		
13		*o*-Cl	205–206	40.7	C	$C_{13}H_{14}ClN_3O_4$	±	
14		*p*-Cl	173–174	38.0	C	$C_{13}H_{14}ClN_3O_4$		
15		*o*-OCH_3	155–156	47.0	A	$C_{14}H_{17}N_3O_5$	+	
16		*p*-OCH_3	129–131	51.0	A	$C_{14}H_{17}N_3O_5$		
17	III	H	99–100	78.0	A	$C_{14}H_{18}N_2O_2$	+	
18		*p*-CH_3	113–114	68.0	D	$C_{14}H_{18}N_2O_2$		
19		*p*-Cl	138–140	66.5	D	$C_{13}H_{15}ClN_2O_2$		
20		*o*-OCH_3	108–109	82.0	D	$C_{14}H_{18}N_2O_3$		

[a] Yields are given for the recrystallized products. [b] A = EtOH–H_2O (1:1), B = EtOH, C = *n*-BuOH, D = cyclohexane–EtOH (2:1). [c] Analytical results obtained for C, H, and N were within ±0.4% of the theoretical values unless listed otherwise. [d] *Anal.* C, N; H: calcd, 5.89; found, 5.44. [e] *Anal.* H, N; C: calcd, 57.72; found, 57.29. [f] Measured by the hot plate method of P. A. J. Janssen and A. Jageneau, *J. Pharm. Pharmacol.*, **9**, 381 (1957), at doses of 30 mg/kg. Data in reference to codeine phosphate as a standard; + means effect prolonging response time of animal 50% above that of standard; ±, 10% above that of standard. [g] Compared with metronidazole, 1:100 g/ml × 10^{-3}; *cf.* F. Kajfež, V. Šunjić, D. Kolbah, T. Fajdiga, and M. Oklobdžija, *J. Med. Chem.*, **11**, 167 (1968).



I

II III

All compounds were prepared by the interaction of the appropriate imidazole with different derivatives, substituted in the ring, of 1,2-epoxy-3-phenoxypropane. In order to obtain derivatives of 5-nitroimidazole (I), formic acid was used in accord with earlier investigations.[10]

Experimental Section[11]

Group I.—2-Methyl-4(5)-nitroimidazole (3.15 g, 0.025 mole) and 0.03 mole of the particular 1,2-epoxy-3-substituted phenoxypropane in 4.9 g (4.0 ml) of formic acid were heated at 90–95° with stirring for 24 hr; 30 ml of 10% HCl was added and heated until all dissolved. On cooling, an oily layer was formed which was separated and extracted with 15 ml of 10% HCl. The acid fractions were combined, extracted ($CHCl_3$), and made basic. Crude products were collected on the filter, washed (H_2O), and recrystallized from solvents listed in Table I. Acidification of the basic filtrate yielded 1.5–1.8 g of unreacted 2-methyl-4(5)-nitroimidazole. Alcohols of the type $CH_2OHCHOHCH_2OC_6H_4X$ have been obtained from the oily residue after extraction with dilute HCl in yields of 20–30% based on the epoxide used.

Group II.—2-Methyl-4(5)-nitroimidazole (3.15 g, 0.025 mole), 0.03 mole of the particular 1,2-epoxy-3-substituted phenoxypropane, and 0.5 ml (0.49 g) of pyridine in 20.0 ml (24 g) of $C_6H_5NO_2$ were stirred and heated to 140°. When a slight evolution of brown gas was observed heating was discontinued for 1 hr. After additional heating at 140–150° for 12 hr $C_6H_5NO_2$ was removed at 0.2 mm. The residue was washed (MeOH), filtered off, and recrystallized.

Group III.—2-Methylimidazole (4.1 g, 0.05 mole) and 0.05 mole of the particular 1,2-epoxy-3-substituted phenoxypropane were refluxed in 8 ml (6.5 g) of *n*-BuOH for 1 hr. The reaction mixture was cooled, 5 ml of cyclohexane was added, and then the mixture was chilled on ice for 48 hr. Crude product was collected on a filter, washed with cyclohexane, and recrystallized.

Acknowledgment.—The authors are grateful to P. Rems for running the infrared spectra, and to Mrs. M. Galonja for the microanalyses.

(10) F. Kajfež, D. Kolbah, M. Oklobdžija, T. Fajdiga, M. Slamnik, and V. Šunjić, *Croat. Chem. Acta*, **39**, 199 (1967).

(11) Melting points were determined on a Kofler hot stage and are corrected. Analyses were performed by the Microanalytical Laboratory, Department of Organic Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb. Where analyses are indicated only by symbols of the elements, analytical results obtained for those elements were within ±0.4% of the theoretical values. Structures of the isomeric compounds of groups I and II were confirmed by nmr and ir spectra.[7]

Topical Mosquito Repellents. II.[1] Repellent Potency and Duration in Ring-Substituted N,N-Dialkyl- and -Aminoalkylbenzamides[2]

H. L. JOHNSON, W. A. SKINNER,

Life Sciences Research, Stanford Research Institute, Menlo Park, California

D. SKIDMORE, AND H. I. MAIBACH

University of California, San Francisco Medical Center, San Francisco, California

Received June 13, 1968

In connection with the acute problem of mosquito transmission of drug-resistant malaria and other dis-

(1) Part I: H. L. Johnson, W. A. Skinner, H. I. Maibach, and T. R. Pearson, *J. Econ. Entomol.*, **60**, 173 (1967).

(2) This work was supported by the U. S. Army Medical Research and Development Command on Contracts DA-40-193-MD-2466 and DA-49-193-MD-2465.

cases, studies were begun in these laboratories on the development of mosquito repellents of long duration. While a systemic repellent might have advantages over a topical one, regardless of the mode of administration of the repellent, the final common area of action is the skin surface. Thus, the factors which affect repellent action at this final point are of equal relevance to topical and systemic agents.

The present studies were aimed at examining the effects of molecular structure and physical properties on the potency and duration of topical repellent action using diethyltoluamide (DEET)[3] as a model structure for effective repellency. To this end several ring-substituted diethylbenzamides[1] were evaluated extensively, on human skin with regard to their repellency to female *Aedes aegypti* mosquitoes. A similar series of ring-substituted aminoalkylbenzamides (including benzoylpiperazines) was prepared in order to broaden the basis of structural comparison. The latter series was selected specifically for study so that the effect of structural changes at the amide nitrogen moiety and the introduction of a basic center could be assessed with regard to repellent efficacy.

Structural aspects of repellency in series I (Table I) were discussed previously; in this series the index of repellency (IR), as determined with a standard quantity of compound in an olfactometer, is directly proportional to volatility[1] as illustrated in Figure 1. The

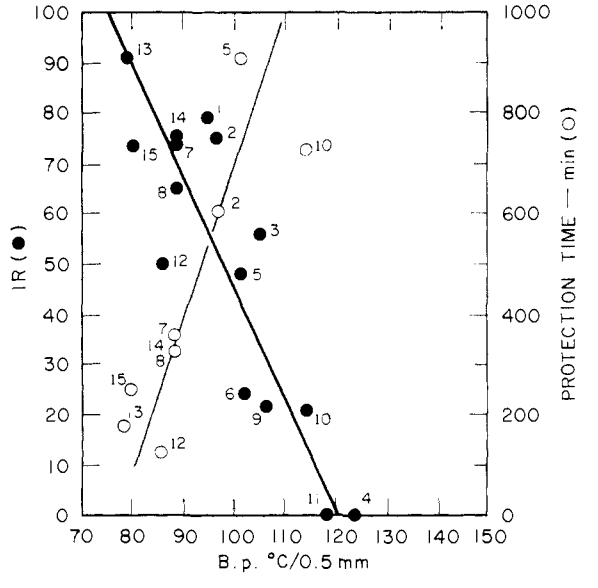


Figure 1.—Relationship of repellency to volatility of N,N-diethylbenzamides. Point numbers refer to compounds listed in Table I (series I). Repellency (●, IR) *vs.* duration (○). Duration data were obtained from initial application to human skin at 0.4 mg/cm² (Table I).

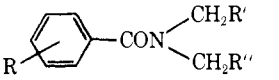
present studies show that, in contrast to the olfactometer results, duration of repellency with these compounds on human skin is inversely proportional to volatility (Figure 1). Thus, diethyltoluamide (I-2) is an effective topical repellent because its volatility is optimum in terms of providing an effective vapor concentration with a minimum rate of evaporative loss. Compounds I-5 and I-10 are of comparable effectiveness in terms of duration; however, in recent tests these compounds exhibited relatively poor resistance to moisture-induced loss from skin. None of the compounds in series II or III exhibited favorable duration properties in comparison with diethyltoluamide.

In the present study repellency was also evaluated in terms of minimum effective quantities (MEQ) of repellent rather than in terms of mosquito response (IR) to vapor from a standard maximum amount of repellent as determined previously.[1] This was done in an attempt to obtain a more practical measure of relative repellent efficacy. In addition to evaporation, systemic absorption is a potential major mode of loss of

(3) E. T. McCabe, W. F. Barthel, S. I. Gertler, and S. A. Hall, *J. Org. Chem.*, **19**, 493 (1954); I. H. Gilbert, H. K. Gouck, and C. N. Smith, *J. Econ. Entomol.*, **48**, 741 (1955).

TABLE I

VOLATILITY AND DURATION OF REPELLENCY OF RING-SUBSTITUTED N,N-DIALKYL- AND -AMINOALKYLBENZAMIDES[a]



Compd	R	Formula[b]	Bp, °C (mm)	Duration, hr[c] A	Duration, hr[c] B
Series I					
1	H	$C_{11}H_{15}NO$	95–97 (0.6)		
2	3-CH_3	$C_{12}H_{17}NO$	94–96 (0.4)	1.5	16
3	4-CH_3	$C_{12}H_{17}NO$	104–106 (0.5)		
4	4-*t*-C_4H_9	$C_{15}H_{23}NO$	125 (0.6)		
5	3,5-CH_3	$C_{13}H_{19}NO$	102 (0.5)	11	15
6	3,4-CH_3	$C_{13}H_{19}NO$	103–104 (0.5)		
7	3-CF_3	$C_{12}H_{14}F_3NO$	87–88 (0.5)	3.5	6
8	3-F	$C_{11}H_{14}FNO$	88–89 (0.6)	3.5	5.5
9	3-Cl	$C_{11}H_{14}ClNO$	106–108 (0.6)		
10	3-Br	$C_{11}H_{14}BrNO$	111–116 (0.6)	5	12
11	3-I	$C_{11}H_{14}INO$	116–118 (0.1)		
12	3,5-CF_3	$C_{14}H_{13}F_6NO$	84–86 (0.6)	1	2
13	2,3,4,5,6-F	$C_{11}H_{10}F_5NO$	79–80 (0.8)	1.5	3
14	2-F	$C_{11}H_{14}FNO$	87–89 (0.5)	3	6
15	4-F	$C_{11}H_{14}FNO$	78–79 (0.3)	3.5	4
16	[d]	$C_{14}H_{21}NO$	65–68 (0.4)		
17	[e]	$C_{11}H_{15}NO$	31–36 (0.1)	2	
18	[f]	$C_{10}H_{13}NO$	42–43 (0.4)	<1	1
19	[g]	$C_{11}H_{13}NO$	36–37 (0.5)	<1	1
Series II					
1	H	$C_{12}H_{18}N_2O$	112–113 (0.6)	0	0
2	3-CH_3	$C_{13}H_{20}N_2O$	112–114 (0.6)	1	3.5
3	2-F	$C_{12}H_{17}FN_2O$	111–112 (0.6)	1	6.5
4	3-F	$C_{12}H_{17}FN_2O$	108–109 (0.65)	1	4.5
5	4-F	$C_{12}H_{17}FN_2O$	111 (0.6)	<1	1
6	2-CF_3	$C_{13}H_{17}F_3N_2O$	114 (0.65)	0	5
7	3-CF_3	$C_{13}H_{17}F_3N_2O$	107–109 (0.65)	3	4
8	4-CF_3	$C_{13}H_{17}F_3N_2O$	110–112 (0.6)	0	1
9	2,3,4,5,6-F	$C_{12}H_{13}F_5N_2O$	98–99 (0.65)	2	6
10	3,5-CF_3	$C_{14}H_{16}F_6N_2O$	102–103 (0.65)	1.5	1
11	[h]	$C_{12}H_{16}N_2O$	55 (0.6)	1	1.5
12	[i]	$C_{12}H_{22}N_2O$	99 (0.6)	1	1
13	[j]	$C_{13}H_{24}N_2O$	99 (0.5)	5.5	6
Series III					
1	H	$C_{12}H_{16}N_2O$	116–119 (0.65)[k]	0	0
2	2-F	$C_{12}H_{15}FN_2O$	121–124 (0.65)	0	1
3	3-F	$C_{12}H_{15}FN_2O$	116–118 (0.6)	0	2.5
4	2-CF_3	$C_{13}H_{15}F_3N_2O$	121–122 (0.65)	0	1.5
5	3-CF_3	$C_{13}H_{15}F_3N_2O$	mp 74–75	0	2
6	2,3,4,5,6-F	$C_{12}H_{11}F_5N_2O$	107–110 (0.65)	0	1.5
7	3,5-CF_3	$C_{14}H_{14}F_6N_2O$	mp 91–91.5	0	1

[a] Series I: R′ = R″ = CH_3; series II: R′ = H, R″ = $CH_2N(CH_3)_2$; series III: R′, R″ = $CH_2N(CH_3)CH_2$. [b] Analytical results were obtained for C, H, and N and were within 0.4% of the theoretical values; results for series I are given in paper I of this series.[1] [c] Repellents were applied at the rate of 0.2 mg/cm² (A) or 0.4 mg/cm² (B). [d] N,N-Diethyleyclohexanecarboxamide. [e] N,N-Diethyl-*n*-butyramide. [f] N,N-Diethylacetamide. [g] N,N-Diethylformamide. [h] N-Methyl-N-(2-dimethylaminoethyl)acetamide. [i] N-Methyl-N-(2-dimethylaminoethyl)cyclohexanecarboxamide. [j] N-Methyl-N-(2-dimethylaminoethyl)octanamide. [k] M. Harfenist [*J. Am. Chem. Soc.*, **76**, 4991 (1954)] reported bp 114–116° (0.04 mm).

topical repellents.[4] Thus the minimum effective quantity (MEQ) was determined in an olfactometer with respect to application to a glass surface, and the minimum effective concentration (MEC) to prevent biting was determined by application to human skin. It was expected that differences in rates of cutaneous absorption and other variables peculiar to skin would be apparent on comparison of results obtained by the two methods. The MEQ values vary little among series I compounds (Table II) and are comparable to

TABLE II

REPELLENCY OF RING-SUBSTITUTED N,N-DIALKYL- AND -AMINOALKYLBENZAMIDES[a]

Compd	MEQ, mg[b]	MEC, mg/2.5 cm²[c]	IR[d]
I-10	<0.1	0.25–0.3	
I-5	<0.1	0.2–0.25	
I-2	<0.1	0.1–0.2	
I-7	0.15–0.2	0.4–0.43	
I-8	0.1–0.15	0.45–0.47	
I-12	>0.5	~1.0	
I-13	>0.35		
II-1			0
II-8	0.3–0.5		54
II-5	0.3–0.5		
II-4	<0.2		57
II-7	<0.2		60
II-10	0.1–0.2		
II-9	0.1–0.2		61
III-3	>0.5		51
III-6	>0.5		70

[a] Within each series, compounds are listed in order of increasing volatility. [b] Total amount of material on a glass surface of uniform size in a dual-port olfactometer (see text and ref 1); MEQ = minimum amount required to give an index of repellency (IR) greater than 15 [IR = (number of mosquitoes on control side minus number on sample side/total number of mosquitoes)100]. [c] Test method on human skin described in text; MEC = minimum concentration on skin required to prevent biting 15 min after application. [d] Index of repellency;[1] values are means of two to three determinations; values for series I compounds are shown in Figure 1.

the value for diethyltoluamide (I-2). The relatively high apparent MEQ value found for the highly volatile I-13 is undoubtedly due to the fact that significant amounts of this compound are lost prior to testing in the MEQ and MEC determinations. Application of such small amounts to the test surface invariably involves the use of a vehicle such as ether or alcohol. Testing is delayed to allow evaporation of the solvent. When this type of procedure is applied to compounds with relatively high volatility the effectiveness of very small quantities is probably missed because of evaporation prior to testing. This interpretation is consistent with the very short duration of effectiveness of this highly volatile compound (Table I and Figure 1). Similar reasoning may apply to some extent in the case of I-12. However, the significantly low IR value[1] for this substance in comparison with other members of this series of similar volatility (Figure 1) suggests that low intrinsic potency is a major factor in the high MEQ and MEC and the extremely short duration of effectiveness of the compound. Of possible significance in this regard is the fact that I-12 is unique in this series in terms of its high relative partition coefficient.[1] The direct relationship of repellency to volatility seen in the case of the diethylbenzamides (Figure 1) is less obvious in the benzoylethylenediamines (II) and the benzoylpiperazines (III). However, the over-all importance of volatility is still apparent. Series II compounds exhibit similar and moderately high IR values while the higher boiling members (**5** and **8**) show high MEQ values (Table II). The still less volatile series III compounds are ineffective on skin at 0.2 mg/cm² (Table I); their MEQ values are thus in the neighborhood of 0.2 mg/cm² although their IR values are moderately high as shown in Table II.

The low repellency inherent in high-boiling materials imposes a limitation on the concept that duration is maximized by low volatility. As illustrated in Figure 2, decreasing volatility resulting, for example, from

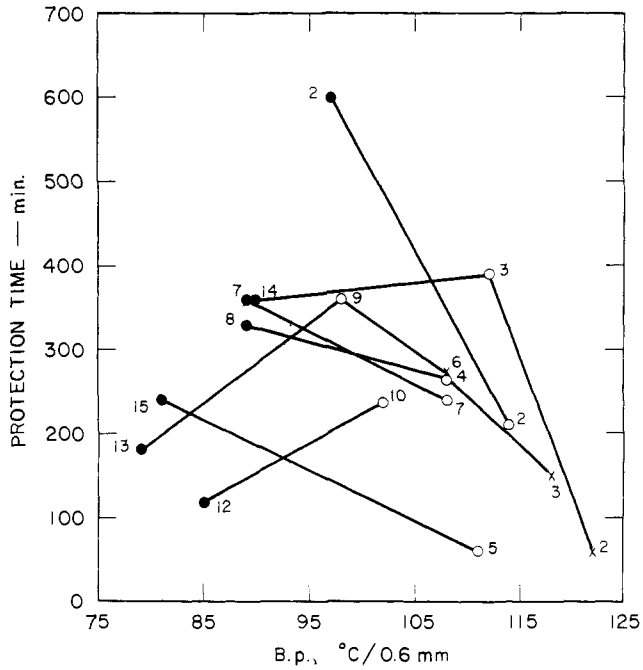


Figure 2.—Duration of effectiveness against mosquito biting *vs.* volatility and structure of topical repellents. Application rate: 0.4 mg/cm². Point numbers for series I (●), series II (○), and series III (X) refer to compounds listed in Table I. Lines connect analogous compounds in the three series (identical ring substituents).

the progressive structural change of series I to series II to series III results in longer duration to a point; further decreases in volatility actually are detrimental to duration due to attendent decreases in effective repellency. A given surface area must be covered more completely (greater repellent surface area) in order to provide sufficient vaporization for an effective vapor concentration. Others[5] have previously concluded that differences in protection periods between repellents are correlated with differences in minimum effective dosage or concentration. The present results indicate that the latter are largely dependent upon differences in volatility.

The above discussion pertains to the *effective* repel-

(4) C. H. Schmidt, F. Acree, and M. C. Bowman, *J. Econ. Entomol.*, **52**, 928 (1959); S. Kasman, L. A. O. Roadhouse, and G. F. Wright, *Mosquito News*, **13**, 116 (1953).

(5) C. N. Smith, I. H. Gilbert, H. K. Gouck, M. C. Bowman, F. Acree, Jr., and C. H. Schmidt, Technical Bulletin No. 1285, Agricultural Research Service, U. S. Department of Agriculture, 1963.

lency of these materials. Such a property is a composite of volatility and intrinsic potency. The latter is presumably dependent upon structure[6] and independent of volatility. In the case of the present compounds minor differences in intrinsic potency are minimized by the dominant importance of volatility. Nonetheless, it is apparent that gross differences in intrinsic potency do exist. Notable is the lack of repellency in II-1 and III-1, whose volatility is comparable to other members of these series. It is also apparent (Table II) that the simple aromatic diethylbenzamides (I) are more potent than the II and III compounds of similar volatility (compare I-2,5,10, bp 96–114° (0.5 mm), with II-5,8, bp 111° (0.6 mm), and III-6, bp 107° (0.6 mm)). Similarly, within series I the relatively low intrinsic repellency of **12** may be cited.

It is of interest that the similarity of MEQ and MEC values (Table II) in series I indicates that differences in duration on skin are not significantly related to differential absorption rates in this series. The present results further emphasize the importance of structure and volatility in determining both repellency and duration of effectiveness of topical repellents. In addition, they indicate that volatility must be considered in both the design and interpretation of results of methods for testing repellency.

(6) J. T. Davies and F. H. Taylor, *Biol. Bull.*, **117**, 222 (1959); T. P. McGovern, M. Beroza, and H. Gouck, *J. Econ. Entomol.*, **60**, 1591 (1967).

Experimental Section

Synthesis.—The compounds (II and III) were synthesized by reaction of the acid chloride of the appropriate substituted benzoic acid with the N,N,N′-trisubstituted diamine in the presence of excess amine. Products were purified and boiling points (uncorrected) were determined by vacuum distillation through a 10-cm Vigreux column. Physical constants are given in Table I. Compounds I-2 and -17–19 were obtained from Eastman Organic Chemicals Co., and before use were distilled as described above.

Biological Evaluation.—Olfactometer determinations of MEQ values were performed by a modification of the method previously described.[3] Sample vapors were delivered to the olfactometer cage by passing air through a 100-ml sample flask to which had been added a known weight of test compound. The test compound was prepared for evaluation by dissolving it in a standard amount of Et_2O; it was then deposited in the flask by spin evaporation of the ether *in vacuo* for a period of 2–3 min. Remaining ether vapors were removed with a brief flushing with N_2. For each compound a series of quantities was tested in order to bracket a weight range which produced a minimum response in terms of mosquito distribution. Female *Aedes aegypti* mosquitoes (5–7 days old) were used exclusively in all tests. Similarly, MEC tests were conducted by uniform application of various amounts of repellent in EtOH to an exposed area of the arm of a human subject. In this manner, a minimum concentration range for prevention of biting was determined by exposure of the treated area to a 0.3 m^3 cage of 100 mosquitoes. Exposure was delayed for 15 min following application in order to allow dissipation of the solvent. Such a procedure was repeated once with each compound and in the repeated tests all compounds were run on the same day. Duration testing was conducted in a similar manner except that application was at the rates of 0.2 and 0.4 mg/cm^2. The treated area was exposed to mosquitoes every 0.5 hr until biting was noted and confirmed during the subsequent exposure. The same test subject was used in all determinations.

New Compounds

Synthesis of N-Aryl-N′-2-thiazolylguanidines

WAHID U. MALIK, P. K. SRIVASTAVA, AND S. C. MEHRA

Department of Chemistry, University of Roorkee, Roorkee, India

Received July 29, 1968

Rose and Swain[1] prepared and studied the biological activities of a series of bisdiguanides; Ram[2] reported some arylguanidines in which one group was substituted benzothiazole and another was a phenyl or substituted-phenyl group and studied their antibacterial properties. Recently some benzothiazolylguanidines were also reported[3] to possess algaecidal properties. It was therefore thought worthwhile to synthesize some additional thiazolylguanidines.

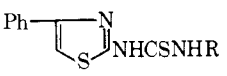
Experimental Section

N-Phenyl-N′-2-(4-phenylthiazolyl)thiocarbamide.—Phenyl isothiocyanate (3 ml) and 2-amino-4-phenylthiazole (5 g) were refluxed for 2 hr. Excess phenyl isothiocyanate and 2-amino-4-phenylthiazole were removed by washing several times (petroleum ether (bp 40–60°), Et_2O). The thiocarbamide thus obtained was crystallized from EtOH, mp 176°, yield 95%. *Anal.* ($C_{16}H_{13}N_3S_2$) N, S.

Similarly, various substituted N-aryl-N′-2-(4-phenylthiazolyl)-thiocarbamides were prepared (see Table I).

TABLE I

N-ARYL-N′-2-(4-PHENYLTHIAZOLYL)THIOCARBAMIDES



No.	R	Mp, °C	Formula[a]
1	*o*-MeC_6H_4	192	$C_{17}H_{15}N_3S_2$
2	*m*-MeC_6H_4	199	$C_{17}H_{15}N_3S_2$
3	*p*-MeC_6H_4	195	$C_{17}H_{15}N_3S_2$
4	*o*-$OMeC_6H_4$	200	$C_{17}H_{15}N_3OS_2$
5	*m*-$OMeC_6H_4$	170	$C_{17}H_{15}N_3OS_2$
6	*p*-$OMeC_6H_4$	190	$C_{17}H_{15}N_3OS_2$
7	*p*-$OEtC_6H_4$	225	$C_{18}H_{17}N_3OS_2$
8	*p*-ClC_6H_4	136	$C_{16}H_{12}ClNS_2$

[a] All compounds analyzed satisfactorily for N, S.

N-Phenyl-N′-2-thiazolylguanidine.—N-Phenyl-N′-2-thiazolylthiocarbamide quantitatively formed N-phenyl-N′-2-thiazolylguanidine when heated with yellow PbO and ethanolic NH_3 in a sealed tube at 110°. The product was crystallized from 50% EtOH, mp 136°. *Anal.* ($C_{16}H_{14}N_4S$) N, S.

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