cooled reaction solution was poured onto 220 g of ice, and the resulting suspension was mixed well with 100 mL of ether. The solid material was filtered off and washed with ether several times. The crude product thus obtained was recrystallized from ethanol.

4-Dodecyl-5-methyl-2-imidazolidinone (6b). Platinum oxide (1.0 g) suspended in 100 mL of acetic acid was activated by exposure to gaseous hydrogen. A solution of **4b** (5.6 g, 0.020 mol) in 300 mL of acetic acid was added to the catalyst solution in one portion. Hydrogenation was carried out at atmospheric pressure for 2 days, and then a small amount of fresh catalyst (0.1 g) was added. Hydrogenation was continued for an additional 2 days. The catalyst was filtered off and washed with hot acetic acid. The filtrate and washings were combined and evaporated in vacuo repeatedly with ethanol and finally to dryness. The crude product was recrystallized from acetone and then from acetonitrile.

When the readdition of catalyst was not done in another run, 4-dodecyl-5-methyl-2-imidazolinone (11) was obtained as a by-product in 8% yield after recrystallization from ethanol twice: mp 228–231 °C; ^{1}H NMR (CF_3CO_2H) δ 0.94 (t, J = 6 Hz, 3 H, CH_3), 1.37 (20 H, CH_2), 2.20 (s, 3 H, 5-CH_3), 2.58 (t, J = 7 Hz, 2 H, 4-α-CH_2), 9.92 (br s, 2 H, NH).

1-Propionyl-4-dodecyl-5-methyl-2-imidazolidinone (9). A 1.2-g (4.5 mmol) sample of **6b** was mixed with 2.3 g (25 mmol) of propionyl chloride in 10 mL of hexane. The reaction mixture was refluxed for 3 h. After the solvent and excess reagent were distilled off, the residue was recrystallized from hexane.

Some physical properties of newly prepared compounds in this work are summarized in Tables I and II.

Acknowledgment. The technical assistance of Messrs. T. Teshima and A. Takezako in the synthesis of some of the compounds is gratefully acknowledged.

Registry No. 1, 5918-93-4; 2, 1192-34-3; **3a**, 71647-94-4; **3b**, 71647-95-5; **4a**, 71672-50-9; **4b**, 71647-96-6; **5a**, 3656-96-0; **5b**, 71647-97-7; **6a**, 71647-98-8; **6b**, 71647-99-9; **7**, 71648-00-5; **8a**, 71648-01-6; **8b**, 71648-02-7; **9**, 71648-03-8; **10**, 71648-04-9; **11** (R_2 = $C_{12}H_{25}$), 71672-51-0; dodecanoyl chloride, 112-16-3; propionyl chloride, 79-03-8; hexanoyl chloride, 142-61-0; methoxycarbonyl chloride, 79-22-1; *p*-nitrophenoxycarbonyl chloride, 7693-46-1; acetonitrile, 75-05-8.

Notes

Photochemistry of 4,6-Diphenyl-2,2-dioxo-1,2,3,5-oxathiadiazine

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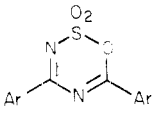
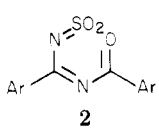
N-Sulfonylamines have been generated as reactive intermediates in solution by the base-induced dehydrochlorination of sulfamoyl chlorides.[1] 4,6-Diaryl-2,2-dioxo-1,2,3,5-oxathiadiazines (**1**), which are readily prepared from aryl nitriles and sulfur trioxide,[2] are potentially attractive precursors to the novel amidine-based *N*-sulfonylamines **2**. Some aspects of the photochemistry of **1** (Ar = Ph) and



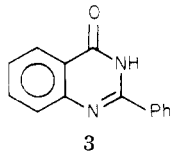
1



2

attempts to establish the intermediacy of **2** (Ar = Ph) in the photochemical transformations of **1** are reported in this paper.

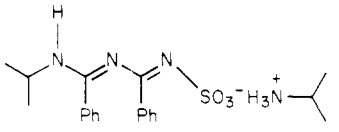
Irradiation (λ >290 nm) of **1** (Ar = Ph) in dichloromethane containing 5% by volume of ethanol or 2-methyl-2-propanol led to complete disappearance of **1**. From the crude photolysate, 2-phenyl-4(3*H*)-quinazolinone (**3**) was isolated in 40–60% yields. Under identical irradiation conditions, but in the absence of added alcohol, **3** was not detected (TLC) and only uncharacterizable materials resulted. The formation of **3** can be rationalized by the mechanism in Scheme I.



3

The ring opening of **1** to **2** and the subsequent trapping by alcohol to give aminosulfonate **4** are analogous to the chemistry observed by de Mayo and co-workers[3] in the irradiation of six-membered ring diene sulfones. de Mayo postulated sulfene intermediates that were intercepted by alcohols to give stable sulfonate esters. In the present study, however, adduct **4** is proposed to undergo further photoexcitation to give a delocalized diradical **5**, which then rearranges to **6**. The observed product **3** finally is formed upon the loss of $ROSO_2H$ from **6**.

All attempts to chemically trap **2** were unsuccessful. Dichloromethane solutions of **1** containing 2,3-dimethyl-2-butene (20× molar excess), ethyl vinyl ether (40×), or dichloroketene ethylene ketal (20×) were irradiated, but cycloadducts analogous to those reported by Burgess[1] were not detected. Potential nucleophilic trapping agents such as isopropylamine rapidly reacted with **1** in the dark to give **7**.[4]



7

In view of the failure to trap **2**, the plausibility of the photochemical conversion of the proposed intermediate **4** to **3** (Scheme I) must be established. Unfortunately, all attempts to independently synthesize **4** (R = CH_2CH_3) were unsuccessful. However, the *N*-tosyl analogue **9** was

(1) G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **94**, 6135 (1972).

(2) P. Eitner, *Ber. Dtsch. Chem. Ges.*, **25**, 461 (1892).

(3) (a) P. de Mayo et al., *Proc. Chem. Soc., London*, 238 (1961); (b) P. de Mayo et al., *Can. J. Chem.*, **41**, 100 (1963).

(4) Alcohols do not react appreciably with **1** at room temperature in the dark. In contrast to the photochemical results, when **1** is refluxed with ethanol benzamidine-*N*-sulfonic acid,[2] $PhC(NH_2)=NSO_3H$, is isolated in 90% yield. No **3** is detected.

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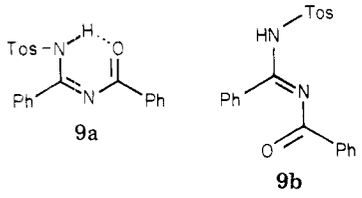
prepared as an isomeric mixture, either by treating the anion of *N*-benzoylbenzamidine (**8**) with tosyl chloride or by refluxing **8** and tosyl chloride in the presence of triethylamine. Two isomers could be isolated in the pure state by fractional crystallization from either ethanol or toluene. The product obtained from toluene (mp 180–183 °C) was assigned the *syn*-hydrogen-bonded structure **9a** based on its IR spectrum (see Experimental Section), while the isomer from ethanol (mp 170–172 °C) appeared to be the anti isomer **9b**.

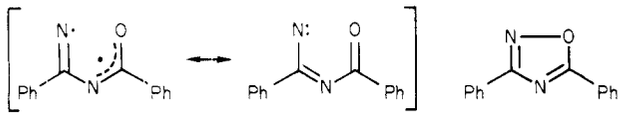


9a

9b

Quinazolinone **3** was indeed produced (66–71% yield, 54–59% conversion) when either **9a** or **9b** was irradiated in dichloromethane. In contrast, both **9a** and **9b** were recovered unchanged after heating 15 h at 140 °C (refluxing xylenes).

An alternative mechanism involving direct extrusion of sulfur dioxide to give **10** followed by rearrangement was also considered, but was rejected. The diradical **10** would be expected to close preferentially to the oxadiazole **11**.



10

However, **11** was not detected in the photolysis of **1** (Ar = Ph), and **11** was recovered unchanged when photolyzed in dichloromethane containing ethanol. Furthermore, this mechanism does not account for the specific role of added alcohol.

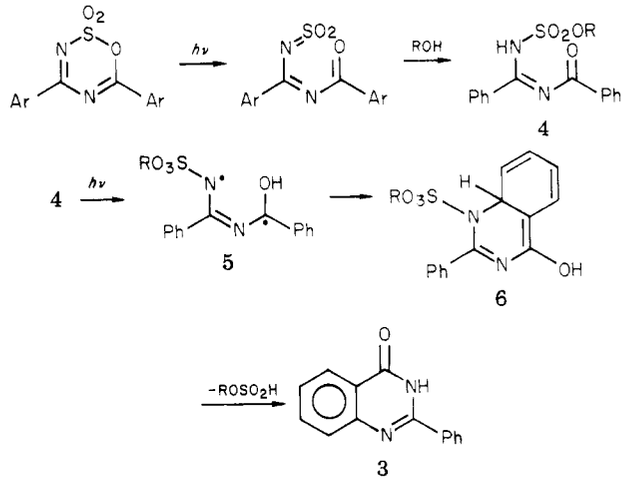
Experimental Section

General. 4,6-Diphenyl-2,2-dioxo-1,2,3,5-oxathiadiazine (**1**, Ar = Ph) [mp 152–153 °C (lit.[2] mp 157–158 °C); UV λ_{max} (CH_2Cl_2) 313 nm (ϵ 28000 M^{-1} cm^{-1})] and ***N*-benzoylbenzamidine** (**8**) [mp 101–102 °C (lit.[2] 105–106 °C, lit.[5] 98–100 °C)] were prepared according to the literature.[2] **3,5-Diphenyl-1,2,4-oxadiazole** (**11**) was prepared by the method of Weidinger and Kranz:[6] mp 98–100 °C (lit. 96–98 °C).

All photolyses were done with a 450-W medium-pressure mercury lamp (Hanovia 679 A 36) in immersion wells equipped with Pyrex filter sleeves. Continuous nitrogen purging was employed and the temperature was maintained at 20–25 °C during the photolysis. Dichloromethane was Fischer reagent (ACS) grade, used as received.

2-Phenyl-4(3*H*)-quinazolinone (**3**). **By Irradiation of 1 (Ar = Ph).** A solution of 0.750 g (2.62 mmol) of **1** (Ar = Ph) in 500 mL of 5% (v/v) ethanol/dichloromethane was placed in a photolysis well and sparged with N_2 for 15 min prior to, and then continuously during, irradiation. After 2.0 h of irradiation the pale-yellow photolysate was concentrated to dryness, and the crude product was triturated with acetonitrile and filtered to afford 320 mg (55%) of **3** as a pale-yellow powder. Recrystallization from acetonitrile gave material identical in all respects with an authentic sample.

By Irradiation of *N*-Tosyl-*N'*-benzoylbenzamidine (**9**). A dichloromethane solution (2.6×10^{-3} M) of **9b** (0.500 g, 1.30 mmol) was irradiated, with N_2 sparging, for 2.0 h and then concentrated to a volume of about 100 mL. The solution was extracted three times with 50 mL of 5% NaOH, and the basic fractions were retained. The organic portion was dried ($MgSO_4$) and concentrated to give 105 mg (35%) of **3** (IR, mp, TLC). From the basic aqueous portion was obtained, after acidification and extraction into CH_2Cl_2, 230 mg (46%) of a mixture of isomers of **9**. The yield of **3** based on unrecovered **9** was 66%.



Similarly, irradiation of isomer **9a** gave **3** (42%) and recovered **9** as an isomeric mixture (41%).

***N*-Tosyl-*N'*-benzoylbenzamidine** (**9**). **A. From *N'*-Benzoylbenzamidine** (**8**), **Tosyl Chloride, and Triethylamine.** A mixture of 4.40 g (20 mmol) of **8**, 4.00 g (21 mmol) of tosyl chloride, 2.80 mL (20 mmol) of triethylamine, and 80 mL of toluene was refluxed for 24 h under nitrogen. The light-brown suspension was cooled and filtered to give 1.53 g (53%) of triethylamine hydrochloride. The filtrate was concentrated to 9.20 g of a brown oil which was taken up in a small amount of ethanol and refrigerated overnight. Filtration gave 1.10 g of crude **9b** (mp 150–155 °C), which was recrystallized from ethanol to afford 1.00 g (13% based on **8**, 26% based on Et_3N·HCl yield) of white needles: mp 170–172 °C; NMR ($CDCl_3$) δ 11.33 (br s, 1 H, NH), 8.1–7.8 (m, 4 H), 7.7–7.2 (m, 10 H), 2.38 (s, 3 H); IR (KBr) 3450 (br), 1710 (s), 1590 (s), 1550 (s), 1330 (s), 1280 (s), 1235 (s), 1155 (s), 1075 (s), 984 (s), 913 (s), 828 (m), 818 (m), 800 (m), 788 (m), 742 (s), 702 (s) cm^{-1}; UV (CH_2Cl_2) 259 nm (ϵ 29000). Anal. Calcd for $C_{21}H_{18}N_2O_3S$: C, 66.65; H, 4.79; N, 7.40; S, 8.47. Found: C, 67.03; H, 4.87; N, 7.35; S, 8.43. The crude product from a similar preparation was taken up in hot toluene. Cooling afforded 2.15 g (28%) of **9a**: mp 180–183 °C; NMR ($CDCl_3$) δ 8.2–7.8 (m, 4 H), 7.7–7.3 (m, 8 H), 7.03 (d, J = 8 Hz, 2 H, part of tolyl A_2B_2), 2.30 (s, 3 H), the NH was not observed; IR (KBr) 3350 (sharp), 1699 (s), 1600 (s), 1560 (s), 1260 (vs), 1215 (s), 1170 (vs), 1120 (s), 1095 (s), 1025 (s), 1005 (s), 812 (m), 803 (m), 770 (s), 706 (s), 678 (s) cm^{-1}. Anal. Found: C, 67.13; H, 4.86; N, 7.36; S, 8.42.

B. From the Anion of 8. A tetrahydrofuran solution of *N'*-benzoylbenzamidine anion at 5 °C generated by reacting a stoichiometric amount of *n*-butyllithium with **8** was treated with 1 equiv of tosyl chloride. After stirring 30 min at room temperature, the mixture was quenched with saturated ammonium chloride solution. Normal workup afforded 90–95% of crude **9**.

1,3,5-Triaza-6-methyl-2,4-diphenylhepta-1,3-diene-1-sulfonic Acid, Isopropylamine Salt (**7**). A solution of 5.7 g (20 mmol) of **1** (Ar = Ph) in 150 mL of dichloromethane was treated in one portion with 10 mL of isopropylamine. The reaction mixture quickly clouded and a copious precipitate formed after 1 h. The mixture was filtered and the filter cake was washed with ether to give 8.1 g (100%) of water-soluble **7**: mp 175–177 °C; NMR (Me_2SO-d_6) δ 1.24 (br t, 12 H), 2.06 (s, 1 H, NH), 3.22 (br m, 1 H), 4.12 (br m, 1 H), 7.0–7.7 (complex m, 10 H). Anal. Calcd for $C_{20}H_{28}N_4O_3S$: C, 59.38; H, 6.98; N, 13.85. Found: C, 59.64; H, 6.92; N, 13.88.

(5) G. Palazzo, G. Strani, and M. Travella, *Gazz. Chim. Ital.*, **91**, 1085 (1961).
(6) H. Weidinger and J. Kranz, *Chem. Ber.*, **96**, 2070 (1963).

Registry No. 1(Ar = Ph), 71734-80-0; **3**, 1022-45-3; **7**, 71734-82-2; **8**, 16776-73-1; **I** Li salt, 71734-83-3; **9a**, 71734-84-4; **9b**, 71734-85-5; tosyl chloride, 98-59-9; isopropylamine, 75-31-0.

Crystal Structure and Stereochemistry of Ivalbin, a Xanthanolide[1]

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Our X-ray analysis of parthemollin (**1**)[2] established the stereochemistry of a number of xanthanolides with a cis-fused γ-lactone ring closed toward C-6[3] and showed that in this series neither the Stöcklin–Waddell–Geissman rule[4] for predicting the nature of the ring fusion from the lactone Cotton effect nor Beecham's suggestion[5] that the sign of the lactone Cotton effect is determined by the chirality of the C=C—C=O chromophore is valid. It was therefore of interest to examine a xanthanolide with a lactone ring closed toward C-8; we selected ivalbin (**2**)[6,7] because some doubt remained[7] about its configuration at C-2.

Crystal data for ivalbin are listed in the Experimental Section. Figure 1 is a stereoscopic drawing of the molecule which shows that our original[7] stereochemical assignments were correct. Figure 1 also represents the absolute configuration for two reasons. (1) Application of the Horeau method to two derivatives of ivalbin showed[7] that its configuration of C-4 was *S*; (2) ivalbin was correlated[6-8] with xanthinin (**3**) without altering the stereochemistry at C-10. Xanthinin, in turn, was degraded to (−)-*S*-methylsuccinic acid. Hence the configuration of ivalbin at C-10 is also *S*.

The lactone ring fusion of ivalbin is trans with H-7α, i.e., it is 7*R*,8*S* as originally deduced[7] on biogenetic grounds and on the basis of the positive Cotton effect in a lactone closed to C-8 (Stöcklin–Waddell–Geissman rule). The analysis thus provides independent evidence for the stereochemistry assigned[8] to C-7 and C-8 of xanthinin and various congeners which have been correlated with ivalbin; the configuration of these compounds at C-2 (and in the case of xanthanol and isoxanthanol, at C-4 as well) remains unknown.

Tables I–IV listing final atomic and final anisotropic thermal parameters, bond lengths, and bond angles of ivalbin are available as supplementary material. Table V lists selected torsion angles. As is also apparent from Figure 1, the cycloheptene ring in the crystal adopts a chair conformation which is slightly distorted from C_s symmetry, possibly as the result of a serious C-10, methyl, C-1 side-chain interaction which would develop in a distorted boat.[9] The ^{1}H NMR coupling constants (see Table VI) indicate that this is also the conformation adopted in solution. The α-methylene γ-lactone ring is much less flattened than in parthemollin, the sum of the internal torsion angles (Table V) being 101° instead of 39°, and deviates significantly from the envelope conformation, with C(8)–O(3)–C(12)–C(11) and O(3)–C(12)–C(7) torsion angles of 11.3 and 8.8° (±0.5°), respectively. The C(13)–C(11)–C(12)–O(4) angle is 10.5°; the chirality of the C=C—C=O chromophore

Table V. Torsion Angles (deg) in Ivalbin[a]

C(10)-C(1)-C(5)-C(6)	−7.5
C(1)-C(5)-C(6)-C(7)	−41.0
C(5)-C(6)-C(7)-C(8)	67.7
C(6)-C(7)-C(8)-C(9)	−80.7
C(7)-C(8)-C(9)-C(10)	76.7
C(11)-C(7)-C(8)-O(3)	30.3
C(7)-C(8)-O(3)-C(12)	−27.0
C(8)-O(3)-C(12)-C(11)	11.3
O(3)-C(12)-C(11)-C(7)	8.8
C(12)-C(11)-C(7)-C(8)	−23.9
C(13)-C(11)-C(12)-O(4)	10.5
C(6)-C(5)-C(1)-C(2)	173.2
C(5)-C(1)-C(2)-C(3)	−107.3
C(1)-C(2)-C(3)-C(4)	173.3
C(2)-C(3)-C(4)-C(15)	−74.1

[a] Estimated standard deviation for a typical C-C-C-C torsion angle is 0.5°.

Table VI. 270-MHz ^{1}H NMR Spectrum of Ivalbin[a,b]

H-2	4.03 dt	H-9a	2.18 ddd
H-3a	1.5 m[b]	H-9b	1.5 m[b]
H-3b	1.37 dt	H-10	2.71 m
H-4	3.64 m	H-13a	5.98 d
H-5	5.69 dd	H-13b	5.59 d
H-6a	2.53 ddd	H-14	1.05 d[c]
H-6b	2.07 ddd	H-15	1.11 d[c]
H-7	2.40 m	2-OH	4.70 d (5)
H-8	4.37 ddd	4-OH	4.43 d (4)

[a] Run in Me_2SO-d_6 with Me_4Si as internal standard. Values in ppm. [b] Superimposed signals. [c] Intensity three protons. *J*'s (in Hz): 2,3a = 2,3b = 4,15 = 10,14 = 7; 5,6a = 10; 5,6b = 3; 6a,6b = 14; 6a,7 = 2; 6b,7 = 11.5; 7,8 = 12; 7,13a = 3.5; 7,13b = 3; 8,9a = 12.5; 8,9b = 2; 9a,9b = 13; 9a,10 = 3.5; 9b,10 = 10.

Table VII. ^{13}C NMR Spectra[a]

carbon	1	2	3	4
1	143.60	150.06	145.12	139.17
2	65.72 d	76.42 d	66.25 d	25.58 t
3	50.73 t	44.60 t	46.77 t	41.03 t
4	206.58	65.08 d	63.26 d	207.10
5	120.52 d	122.64 d	119.49 d	123.52 d
6	78.65 d	24.73 t	78.91 d	78.02 d
7	37.85 d	48.28 d	38.13 d	38.90 d
8	28.32 d	82.35 d	28.48 t	34.68 t
9	29.77 t	36.79 t	30.20 t	72.48 d
10	32.41 d	28.72 d	32.76 d	33.91 d
11	139.83	139.96	139.14	139.95
12	169.30	169.65	169.36	169.03
13	122.15 t	118.21 t	121.86 t	122.50 t
14	16.48 q	19.50 q	16.56 q	13.51 q
15	30.46 q	23.94 q	24.13 q	29.57
Ac				170.11, 20.96 q

[a] Run in Me_2SO-d_6 at 67.09 MHz with Me_4Si as internal standard. Frequencies are in ppm. All unmarked signals are singlets.

(1) Work at the Florida State University was supported by a grant (CA-13121) from the U.S. Public Health Service through the National Cancer Institute.

(2) (a) Sundararaman, P; McEwen, R. S.; Herz, W. *Tetrahedron Lett.* **1973**, 3809. (b) Sundararaman, P; McEwen, R. S. *J. Chem. Soc., Perkin Trans. 2* **1975**, 440.

(3) In ref 2a through an error in drawing, the C-2 configurations of apachin and ivambrin which are 2*S*, 4*R*, 6*S*, and 10*S*, were incorrectly shown as 4*S*.

(4) Stöcklin, W.; Waddell, T. G.; Geissman, T. A. *Tetrahedron* **1970**, *26*, 2397.

(5) Beecham, A. F. *Tetrahedron* **1972**, *28*, 5543.

(6) Herz, W.; Chikamatsu, H.; Viswanathan, H.; Sudarsanam, V. *J. Org. Chem.* **1967**, *32*, 682.

(7) Chikamatsu, H.; Herz, W. *J. Org. Chem.* **1973**, *38*, 585.

(8) Winters, T. E.; Geissman, T. A.; Safir, D. *J. Org. Chem.* **1969**, *34*, 153.

(9) Such an interaction has been invoked[2b] to explain the observation that the cycloheptene ring of parthemollin adopts a slightly distorted C_s-boat rather than a twist-boat conformation.

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