with concentrated hydrochloric acid and extracted with ether, and the organic extracts were washed with water and saturated salt solution, dried over sodium sulfate, and evaporated to dryness. The residue was taken up in toluene, and the solution was filtered and concentrated to yield 2.85 g (13.6%) of **8a**, mp 154.4 °C. The IR and NMR spectra were identical with the spectra of **8a** prepared by the first procedure.

1-(4-Chloro-2-methylphenyl)-5-methyl-2-thiobiuret (8b). By the same procedure as that used for the preparation of **8a**, 87.0 g (0.250 mol) of **7b** yielded 50.2 g (78.0%) of **8b**: mp 177.8 °C; NMR (Me_2SO-d_6) δ 2.20 (s, 3, aryl CH_3), 2.68 (d, 3, NCH_3), 6.82 (q, 1, NH), 7.1–7.85 (m, 3, aromatic), 10.15 (s, 1, NH), 12.07 (s, 1, NH).

Anal. Calcd for $C_{10}H_{12}ClN_3OS$: C, 46.60; H, 4.69; N, 16.30. Found: C, 46.80; H, 4.73; N, 16.09.

2-Methyl-5-(phenylamino)-1,2,4-thiadiazol-3(2*H*)-one (9a).[22] To 4.18 g (20.0 mmol) of **8a** in 100 mL of absolute ethanol was added 3.20 g (20.0 mmol) of bromine while the solution was cooled in an ice bath. Ice was added immediately and the precipitate collected. Recrystallized from 1.8 L of acetonitrile gave 2.75 g (66.4%) of **9a**: mp 206.1 °C; NMR (Me_2SO-d_6) δ 3.13 (s, 3, NCH_3), 7.1–7.8 (m, 5, aromatic), 10.75 (very broad, 1, NH); IR (Nujol) 1635 cm^{-1}.

Anal. Calcd for $C_9H_9N_3OS$: C, 52.16; H, 4.38; N, 20.27. Found: C, 52.30; H, 4.42; N, 20.54.

Preparation of 3a from 9a. To 518 mg (2.50 mmol) of **9a** suspended in 20 mL of THF was added 5 drops of triethylamine and 1.00 mL (17.0 mmol) of methyl isocyanate. After 1 h, the solution was evaporated to dryness, and the residue was recrystallized from benzene to yield 475 mg (71.9%) of **3a**: mp 192.4 °C; IR and NMR spectra were identical with the spectra for **3a** prepared as described above from **1a** and methyl isocyanate.

5-[(4-Chloro-2-methylphenyl)amino]-2-methyl-1,2,4-thiadiazol-3(2*H*)-one (9b).[22] By the same procedure as that used for the preparation of **9a**, 2.91 g (11.3 mmol) of **8b** yielded 1.75 g (60.6%) of **9b**, mp 190.6 °C, after recrystallization from ethanol: NMR (Me_2SO-d_6) δ 2.26 (s, 3, aryl CH_3), 3.08 (s, 3, NCH_3), 7.15–7.9 (m, 4, aromatic and NH); IR (Nujol) 1631 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}ClN_3OS$: C, 46.97; H, 3.94; N, 16.43. Found: C, 47.23; H, 3.98; N, 16.56.

(22) The oxidative cyclization of 1-substituted-2-thiobiurets by this method is described by F. Kurzer and S. A. Taylor, *J. Chem. Soc.*, 379 (1958).

Preparation of 3b from 9b. To 1.02 g (4.00 mmol) of **9b** in 20 mL of THF was added 5 drops of triethylamine and 1.00 mL (17.0 mmol) of methyl isocyanate. After 1 h, the solution was evaporated to dryness, and the residue was recrystallized from methanol to yield 0.97 g (78%) of **3b**: mp 206.4 °C; IR and NMR spectra were identical with the spectra for **3b** prepared as described above from **1b** and methyl isocyanate.

5-(*N*-Methylanilino)-1,2,3,4-thiatriazole (15). To 9.06 g (50.0 mmol) of 4-methyl-4-phenylthiosemicarbazide was added 125 mL of acetic acid, the suspension was heated to 65 °C and cooled in ice, and 3.57 g (50.7 mmol) of sodium nitrite in 15 mL of water was added at 15–18 °C. The solution was poured into 750 mL of ice–water, and the precipitate was collected, dried, and recrystallized from cyclohexane to yield 5.01 g (52.1%) of **15**, mp 56.3 °C (lit.[5] mp 56–7 °C). A second crop, mp 55.4 °C, 1.89 g (19.7%), was obtained.

Attempted Reaction of 15 with Methyl Isocyanate. To 1.92 g (10.0 mmol) of **15** in 10 mL of THF was added 5 drops of triethylamine and 1.00 mL (17.0 mmol) of methyl isocyanate. After 18 days at room temperature, the solution was evaporated. TLC (4:1 benzene–ethyl acetate) showed only **15**; the IR spectra was identical with that for **15**.

Attempted Reaction of 16 with Methyl Isocyanate. To 2.20 g (10.0 mmol) of *N*-(1,2,3,4-thiatriazol-5-yl)acetanilide (**16**)[23] in 20 mL of THF was added 0.80 mL (14 mmol) of methyl isocyanate and 5 drops of triethylamine. After 11 days at room temperature, only **16** and a trace of acetanilide could be detected by NMR spectroscopy.

Acknowledgment. We thank the Physical and Analytical Chemistry Unit of The Upjohn Co. for the elemental analyses.

Registry No. 1a, 13078-30-3; **1b**, 71582-24-6; **1c**, 52098-72-3; **2a**, 624-83-9; **2b**, 103-71-9; **3a**, 71549-48-9; **3b**, 71549-49-0; **3c**, 71549-50-3; **3d**, 71549-51-4; **5a**, 103-85-5; **5b**, 63980-71-2; **6a**, 28269-82-1; **7a**, 71549-52-5; **7b**, 71549-53-6; **8a**, 71549-54-7; **8b**, 71549-55-8; **9a**, 71549-56-9; **9b**, 71549-57-0; **15**, 71549-58-1; **16**, 42105-60-2; 4-(4-chloro-2-methylphenyl)-3-thiosemicarbazide, 61335-37-3; 4-chloro-2-methylphenyl isothiocyanate, 23165-53-9; hydrazine hydrate, 7803-57-8; benzyl chloride, 100-44-7; 4-methyl-4-(phenylthio)semicarbazide, 21076-11-9; 2-(4-chloro-2-methylphenyl)-3-methyl-4-thiazolidone, 71549-59-2; *N*-methylurea, 598-50-5.

(23) E. Lippmann, D. Reifegerste, and E. Kleinpeter, *Z. Chem.*, **13**, 134 (1973).

Preparation and Reactions of Some Derivatives of 2,4-Benzodiazepines and 1,3-Diazepines

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Some 3-methylene- and 3-benzylidene-2,4-benzodiazepine-1,5-diones **1** and 2-methylene-1,3-diazepine-4,7-diones **2** and the related systems **4** and **5** were prepared by reacting *o*-phthaloyl chloride, succinyl chloride, furan-3,4-dicarbonyl chloride and 1-phenyl-2,5-dimethylpyrrole-3,4-dicarbonyl chloride, respectively, with *N,N'*-diarylacetamidines. 3-Phenylimino derivatives of **1** and **2** and a 3-(phenylimino)-2,4-benzodiazepin-1-one (**8**) were synthesized by treatment of *o*-phthaloyl chloride, succinyl chloride, and *o*-chloromethylbenzoyl chloride with 1,2,3-triphenylguanidine. The 3-methylene- and 3-benzylidene groups of **1** were reduced by catalytic hydrogenation to give 3-alkyl-1*H*-2,4-benzodiazepine-1,5-diones **3**. 2,3,4,5-Tetrahydro-2,4-diphenyl-3-(phenylimino)-1*H*-2,4-benzodiazepin-1-one (**8**) in polyphosphoric acid underwent a remarkable isomerization to 11-oxo-*N,N'*-diphenyl-5(6*H*)-morphanthridinecarboxamidine (**9**) in 95% yield.

Recently we communicated that treatment of *N,N'*-diphenylacetamidine with *o*-phthaloyl chloride and succinyl chloride formed the 3-methylene-2,4-benzodiazepine-1,5-dione **1a** and the 2-methylene-1,3-diazepine-4,7-dione **2a** (Scheme I).[1] Previous to our study, only one other example of a 2,4-benzodiazepinedione was known, and that a 1,3-dione.[2] We now report that the reaction of *N,N'*-diarylacetamidines with various diacyl halides is

(1) H. W. Heine and C. Tintel, *Tetrahedron Lett.*, 23 (1978).
(2) A. M. Felix and R. I. Fryer, *J. Heterocycl. Chem.*, **5**, 291 (1968).

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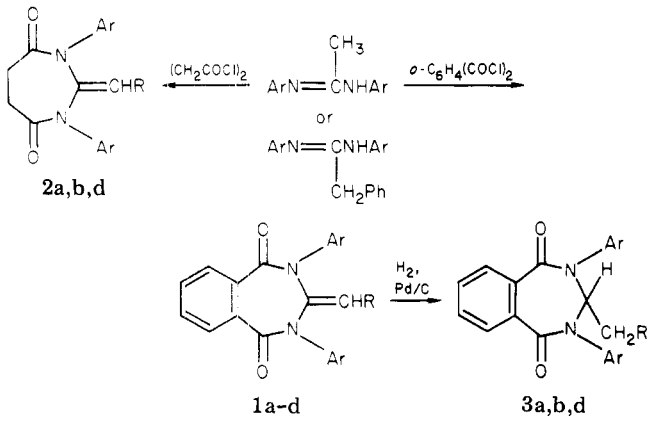
Scheme I



2a,b,d

1a-d

3a,b,d

a, Ar = Ph, R = H
b, Ar = p-BrC_6H_4, R = H
c, Ar = p-$EtOC_6H_4$, R = H
d, Ar = R = Ph

an excellent entry to **1** and **2** and similar systems. 3-Phenylimino derivatives of **1** and **2** and a 3-(phenylimino)-3,4-benzodiazepin-1-one can be prepared by reacting 1,2,3-triphenylguanidine with o-phthaloyl chloride, succinyl chloride, and o-chloromethylbenzoyl chloride, respectively. Some of these 2,4-benzodiazepine derivatives undergo unusual isomerizations or fragmentations when they are reacted with polyphosphoric acid or heated in decalin.

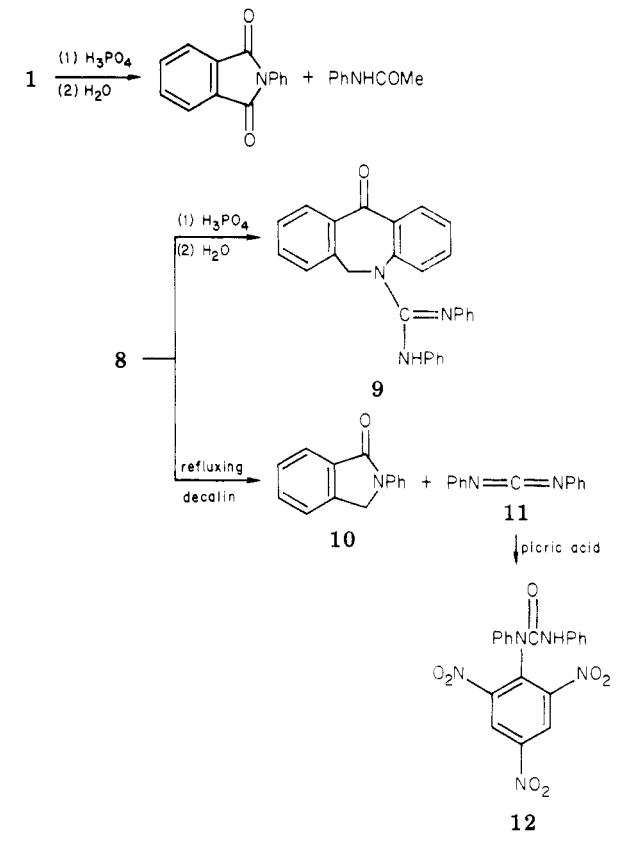
Results

Compounds **1b–d** and **2b,d** were prepared in high yield by admixing in ether containing triethylamine either o-phthaloyl chloride or succinyl chloride with N,N'-bis(p-bromophenyl)acetamidine, N,N'-bis(p-ethoxyphenyl)-acetamidine, or N,N'-diphenyl-α-phenylacetamidine (Scheme I). All the products were characterized by NMR and IR spectroscopy, mass spectrometry and elemental analyses. The NMR spectra for **1a–d** and **2a,b,d** clearly exhibited the 3-methylene or 3-benzylidene protons in the olefinic region. The mass spectra of **1a–c** and **2a,b** showed the appropriate molecular ion and as well an intense peak corresponding to the loss of $ArN{=}C{=}CH_2$ from the molecular ion. The fragmentation pattern of **1d** was similar to **1a–c** with the exception of an intense peak at m/e 193 which represents the loss of N-phenylphenylketenimine. Further evidence for the structure of **1a–d** was provided by their hydrogenation. The products **3a,b,d** were obtained (Scheme I). The NMR spectra of **3a,b** suggested the compounds exist in two conformations. Thus, the spectrum of **3a** exhibited two doublets for the methyl group at δ 1.06 and δ 1.66 ppm. The methine proton of **3a** appeared as two quartets at δ 5.24 and 6.06 and the phenyl groups appeared as two singlets at δ 7.32 and 7.35. The typical AA'BB' splitting pattern for an ortho-substituted benzene ring was seen at δ 7.67 and 8.08. The molecular ion of **3a** was m/e 342 with the parent peak at m/e 223. The latter peak was assigned to N-phenylphthalimide. Another strong peak at m/e 119 most probably represented the imine $PhN{=}CHCH_3$.

Reaction of furan-3,4-dicarbonyl chloride and 1-phenyl-2,5-dimethylpyrrole-3,4-dicarbonyl chloride with N,N'-diphenylacetamidine gave **4** and **5** in yields of 87 and 76%, respectively. The mass spectra of **4** and **5** showed the respective molecular ions and, like **1a**, an intense peak at 117 mass units lower than the molecular ion, representing the loss of N-phenylketenimine.

3-Phenylimino analogues of **1** and **2**, namely **6** and **7**, were obtained when o-phthaloyl chloride and succinyl chloride were reacted with 1,2,3-triphenylguanidine. Similarly, treatment of o-chloromethylbenzoyl chloride with 1,2,3-triphenylguanidine led to the 2,4-benzodiazepine **8**.

Scheme II

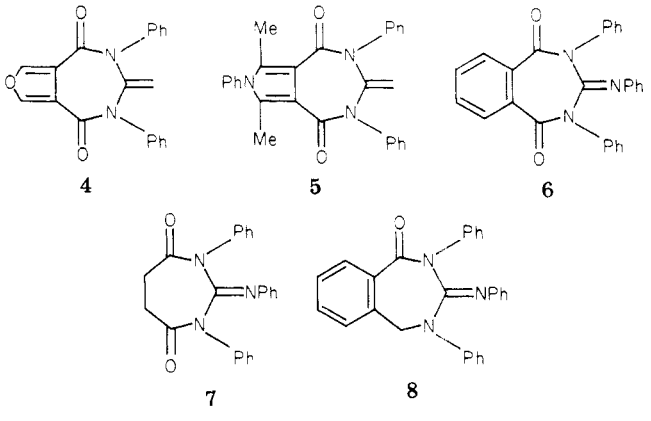


9

10

11

12



4

5

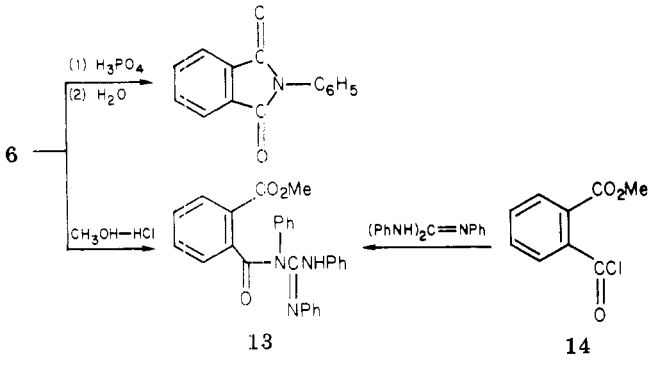
6

7

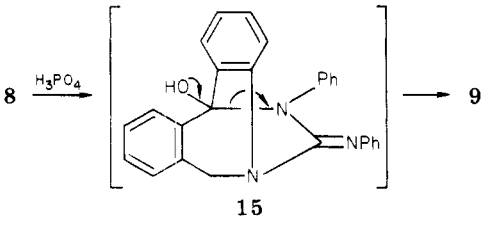
8

We had observed earlier that dissolution of **1a** in hot polyphosphoric acid followed by pouring the reaction mixture on ice gave N-phenylphthalimide and acetanilide (Scheme II). Compound **8** under analogous conditions underwent a novel isomerization to the morphanthridine **9** in 95% yield (Scheme II). Structure proof of **9** rested upon spectral and chemical evidence. The mass spectrum of **9** showed the molecular ion m/e 403 and the solution IR ($CDCl_3$) spectrum shows an NH absorption band at 3450 cm^{-1} and a ketone absorption band at 1625 cm^{-1}. Dibenzocycloheptadienone has virtually the same absorption band. Proton NMR spectroscopy ($CDCl_3$) revealed the presence of the methylene protons as a sharp singlet at δ 5.00 ppm and an exchangeable proton centered at δ 5.5. The ^{13}C NMR spectrum exhibited a signal at 190.4 ppm consistent with a ketone carbonyl between two aryl groups and the presence of two monosubstituted phenyl rings bearing electron-donating groups. In addition, the ^{13}C NMR spectrum showed eight hydrogen bearing sp^2 carbons.[3] In refluxing decalin, **8** was converted into 2-

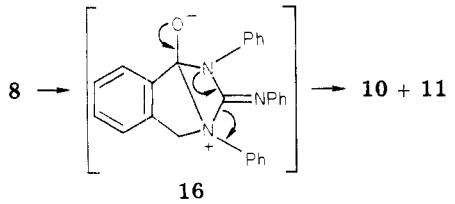
Scheme III



Scheme IV



Scheme V



phenylphthalimidine (10) and diphenylcarbodiimide (11) in yields of 83 and 78%, respectively (Scheme II). The carbodiimide was isolated as the urea 12 after reaction with picric acid.[4]

Compound 6 in hot polyphosphoric acid like 1a formed *N*-phenylphthalimide in 95% yield (Scheme III). In refluxing decalin for 132 h, 6 was again converted into *N*-phenylphthalimide (56%). Heating of 6 in methanol containing a few drops of hydrochloric acid gave 13. The structure 13 was proved by an alternate synthesis from *o*-carbomethoxybenzoyl chloride (14) with 1,2,3-triphenylguanidine (Scheme III).

Discussion

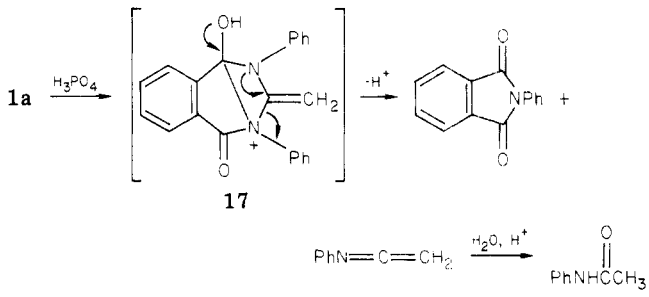
The reaction of various diacyl chlorides with appropriately substituted amidines and guanidines is an excellent method to prepare 3-methylene-2,4-diaryl-1*H*-2,4-benzodiazepine-1,5(2*H*)-diones (e.g., **1a–d**) and similar systems (**2a,b,d,4–7**). Furthermore, the 3-methylene or 3-phenylmethylene moieties of **1a–d** can be reduced to form still another series of 2,4-benzodiazepine-1,5(2*H*)-dione derivatives **3a,b,d**.

We suggest that the novel rearrangement of 8 to the morphanthridine 9 proceeds by an internal Friedel–Crafts reaction in which the intermediate 15 is formed and subsequently converted to 9 (Scheme IV). A rationale for the thermolysis of 8 assumes the formation of 16, followed by fragmentation into *N*-phenylphthalimidine (10) and diphenylcarbodiimide (11) (Scheme V). It is of interest to note that the tendency of 8 in refluxing decalin to be transformed into 10 and 11 apparently also exists under the conditions of mass spectrometry. The mass spectrum

(3) ^{13}C NMR was obtained and interpreted by Robert A. Reamer, Merck Sharp & Dohme Laboratories, Rahway, NJ.

(4) M. Bush, G. Blume, and E. Pungs, *J. Prakt. Chem.*, **79**, 513 (1909).

Scheme VI



of 8 not only exhibits a signal for the molecular ion at *m/e* 403 but also exhibits strong signals at *m/e* 209 and 194 which most probably can be assigned to 10 and 11, respectively.

A similar mechanism and intermediate can be put forth for the reaction of **1a** and 6 in polyphosphoric acid. Thus, protonation of the amido group of **1a** can lead to formation of 17 and 17 can fragment into *N*-phenylphthalimide and *N*-phenylketenimine. The ketenimine under the reaction conditions employed adds water to afford acetanilide (Scheme VI).

Experimental Section

2,4-Bis(4-bromophenyl)-3,4-dihydro-3-methylene-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (1b). To a stirred solution of 1.47 g (0.004 mol) of *N,N'*-bis(4-bromophenyl)acetamidine and 0.91 g (0.009 mol) of Et_3N in 250 mL of anhydrous ether was added a solution of 0.81 g (4 mmol) of *o*-phthaloyl chloride in 50 mL of Et_2O. The reaction mixture was stirred overnight and filtered. Evaporation of the Et_2O gave 1.95 g (98%) of crude **1b** (mp 125–131 °C). Recrystallization from MeOH afforded **1b** (1.61 g, 81%), melting at 175–176 °C. Anal. Calcd for $C_{22}H_{14}Br_2N_2O_2$: C, 53.01; H, 2.83; N, 5.64. Found: C, 53.04; H, 2.82; N, 5.37.

2,4-Bis(4-ethoxyphenyl)-3,4-dihydro-3-methylene-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (1c). A solution of 0.81 g (0.004 mol) of *o*-phthaloyl chloride in 50 mL of Et_2O was added to a mixture of 1.10 g (0.004 mol) of *N,N'*-bis(4-ethoxyphenyl)acetamidine and 0.91 g (0.009 mol) of Et_3N in 200 mL of Et_2O. The mixture was stirred 4 h and filtered. An aqueous suspension of the solid material was extracted well with Et_2O. The ether layer was dried over $MgSO_4$, filtered, and evaporated. There was obtained 1.63 g (95%) of crude **1c**, which when recrystallized from methanol melted at 179–181 °C. Anal. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.88; H, 5.65; N, 6.54. Found: C, 72.69; H, 5.79; N, 6.76.

3-Benzylidene-3,4-dihydro-2,4-diphenyl-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (1d). A 1-L Erlenmeyer flask equipped with a magnetic stirrer was charged with 5.0 g (0.017 mol) of *N,N'*-diphenyl-α-phenylacetamidine, 500 mL of Et_2O, and 3.6 g (0.036 mol) of Et_3N. To the stirred mixture was added a solution of 3.55 g (0.017 mol) of *o*-phthaloyl chloride in 50 mL of dry Et_2O. The solution was stirred for 3 h and filtered. The precipitate was added to CH_2Cl_2. The methylene chloride solution was washed with a saturated sodium chloride solution and water and then was dried over $MgSO_4$. Evaporation of the CH_2Cl_2 left behind 3.95 g of crude **1d**. An additional 3.05 g of crude **1d** was obtained by evaporation of the original ether filtrate. The total yield of crude **1d** (mp 170–172 °C) was 7.0 g (96.3%). Three recrystallizations from MeOH gave 5.16 g (71%) of **1d**, mp 182–183 °C. Anal. Calcd for $C_{28}H_{20}N_2O_2$: C, 80.74; H, 4.84; N, 6.73. Found: C, 80.82; H, 4.79; N, 6.72.

1,3-Bis(4-bromophenyl)tetrahydro-2-methylene-1*H*-1,3-diazepine-4,7-dione (2b). To a stirred solution of 1.47 g (0.004 mol) of *N,N'*-bis(4-bromophenyl)acetamidine and 0.4 g (0.004 mol) of Et_3N in 250 mL of Et_2O was added 0.62 g (0.004 mol) of succinyl chloride in 50 mL of Et_2O. After 10 min an additional 0.51 g of Et_3N in 25 mL of Et_2O was added to the reaction mixture. Three hours later the mixture was filtered and the product washed with H_2O to dissolve the formed Et_3N·HCl. The crude **2b** was combined with the remainder of the **2b** obtained by evaporation of the ether filtrate. The **2b** (mp 119–127 °C) weighed 1.64 g (91%) and when recrystallized from 3:1 MeOH–H_2O gave 1.2 g

(66%) of **2b** (mp 175–176 °C), molecular ion *m/e* 450. Anal. Calcd for $C_{18}H_{14}Br_2N_2O_2$: C, 48.01; H, 3.13. Found: C, 47.87; H, 3.38.

2-Benzylidenetetrahydro-1,3-diphenyl-1*H*-1,3-diazepine-4,7-dione (2d). To a stirred solution of 2.15 g (0.0075 mol) of *N,N'*-diphenyl-α-phenylacetamidine and 1.72 g (0.017 mol) of Et_3N in 500 mL of Et_2O was added 1.16 g (0.0075 mol) of succinyl chloride in 75 mL of Et_2O. The reaction mixture was filtered after 2 h and the filtrate was evaporated to yield 1.45 g (53%) of crude **2d** as a brown oil. Recrystallization from methanol gave **2d**, melting at 165–168 °C. Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.23; H, 5.47; N, 7.60. Found: C, 78.29; H, 5.44; N, 7.56.

3,4-Dihydro-2,4-diphenyl-3-methyl-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (3a). To a 500-mL hydrogenation bottle was added 0.20 g of palladium catalyst (palladium on activated carbon 10% Pd, purchased from Alfa Products), 150 mL of CH_3OH, and 2.15 g (0.0063 mol) of **1a**.[1] The reaction mixture was shaken and heated gently under 55 psig of hydrogen for 24 h. The reaction mixture was filtered through Filter-Aid and the solvent evaporated. There was obtained 1.90 g (88.4%) of **3a**. Two recrystallizations from methanol gave **3a**, melting at 238–240 °C. Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.16; H, 5.30; N, 8.18. Found: C, 76.88; H, 5.17; N, 8.34.

2,4-Bis(4-bromophenyl)-3,4-dihydro-3-methyl-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (3b). Compound **3b** was prepared analogously to **3a** except for a reaction time of 5 days. A 60% yield of **3b** (mp 201–202 °C) was obtained which melted at 231–232 °C after recrystallization from methanol. No analysis is available for **3b**, but the NMR and IR spectra were consistent with the proposed structure.

3,4-Dihydro-2,4-diphenyl-3-(phenylmethyl)-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (3d). Compound **3d** was prepared following the procedure for obtaining **3a**. The reaction time was 24 h. From 2.00 g (0.048 mol) of **1d** was obtained 1.90 g (94%) of **3d** which melted at 189–191 °C after recrystallization from methanol. Anal. Calcd for $C_{28}H_{22}N_2O_2$: C, 80.36; H, 5.30; N, 6.70. Found: C, 80.08; H, 5.64; N, 6.78.

3,4-Dihydro-3-methylene-2,4-diphenyl-1*H*-furo[3,4-*e*][1,3]diazepine-1,5(2*H*)-dione (4). A mixture of 2.0 g (0.013 mol) of furan-3,4-dicarboxylic acid and 20 g (0.168 mol) of thionyl chloride and 15 mL of dry benzene was refluxed for 2.5 h. The residue obtained after the removal of the benzene and excess thionyl chloride by vacuum distillation was dissolved in some dry benzene. The benzene solution of the furan-3,4-dicarbonyl chloride was added to a stirred mixture of 2.7 g (0.013 mol) of *N,N'*-diphenylacetamidine and 2.7 g (0.027 mol) of Et_3N. The reaction mixture was filtered after 4 h and the benzene evaporated. The 3.7 g (86%) of crude **4** (mp 179–181 °C) after recrystallization from methanol melted at 186–188 °C (3.3 g, 76%). Anal. Calcd for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.59; H, 4.33; N, 8.43.

3,4-Dihydro-6,8-dimethyl-3-methylene-2,4,7-triphenylpyrrolo[3,4-*e*][1,3]diazepine-1,5(2*H*,7*H*)-dione (5). A mixture of 1.65 g (0.0064 mol) of 2,5-dimethyl-1-phenylpyrrole-3,4-dicarboxylic acid and 21 g (0.176 mol) of thionyl chloride was heated on a steam bath for 2 h, the residual thionyl chloride removed by vacuum distillation and the crude residue of 2,5-dimethyl-1-phenylpyrrole-3,4-dicarbonyl chloride was dissolved in a small quantity of benzene. This benzene solution was added to a solution of 1.34 g (0.0064 mol) of *N,N'*-diphenylacetamidine and 1.40 g (0.014 mol) of Et_3N. The reaction mixture was refluxed for 4 h and then after cooling was filtered. The filtrate was evaporated and the residue slurried with a small amount of MeOH and filtered. The 2.12 g (76.8%) of **5** (mp 218–224 °C) was purified by running it through a silica gel column employing $CHCl_3$ as the eluting solvent. Recrystallization from methanol of the material obtained from evaporating the $CHCl_3$ eluant gave **5**, melting at 235–237 °C. Anal. Calcd for $C_{28}H_{23}N_3O_2$: C, 77.58; H, 5.35; N, 9.69. Found: C, 77.92; H, 5.38; N, 9.72.

3,4-Dihydro-2,4-diphenyl-3-(phenylimino)-1*H*-2,4-benzodiazepine-1,5(2*H*)-dione (6). To a stirred solution of 2.87 g (0.010 mol) of 1,2,3-triphenylguanidine and 2.23 g (0.02 mol) of Et_3N in 200 mL of Et_2O was added 2.03 g (0.01 mol) of *o*-phthaloyl chloride in 75 mL of Et_2O. The reaction mixture was stirred for 2 h and filtered. The precipitate was added to water to dissolve the Et_3N·HCl and 2.94 g of the insoluble **6** (mp 213–216 °C) was filtered. The ether filtrate was evaporated to give an additional 1.23 g of **6** (total yield 99%). Recrystallization from 1-propanol gave **6** (3.49 g, 84%), melting at 217.5–219 °C. Anal. Calcd for $C_{27}H_{19}N_3O_2$: C, 77.70; H, 4.59; N, 10.07. Found: C, 77.56; H, 4.87; N, 10.05.

Tetrahydro-1,3-diphenyl-2-(phenylimino)-1*H*-1,3-diazepine-4,7-dione (7). A solution of 0.78 g (0.005 mmol) of succinyl chloride in 50 mL of Et_2O was added to a stirred mixture of 1.44 g (0.005 mmol) of 1,2,3-triphenylguanidine and 1.11 g (0.010 mol) of Et_3N in 350 mL of Et_2O. The reaction mixture was stirred for 2 h and filtered. The ether filtrate was evaporated to give 0.61 g (33%) of crude **7** as a yellow gum. Recrystallization from 1-propanol gave 0.51 g (28%) of **7** (mp 176–177 °C). Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.77; H, 5.18; N, 11.38. Found: C, 74.65; H, 4.87; N, 11.66.

2,3,4,5-Tetrahydro-2,4-diphenyl-3-(phenylimino)-1*H*-2,4-benzodiazepin-1-one (8). A 2-L round-bottomed flask was charged with 3.44 g (0.012 mol) of 1,2,3-triphenylguanidine and 4.85 g (0.048 mol) of Et_3N in 1.2 L of reagent grade acetone. To this mixture was added with stirring 2.27 g (0.012 mol) of *o*-chloromethylbenzoyl chloride. The reaction mixture was refluxed overnight, cooled, and filtered. The acetone was evaporated and the residue dissolved in CH_2Cl_2. The methylene chloride solution was washed with H_2O and a solution saturated with NaCl, dried over $MgSO_4$, filtered, and evaporated. The crude **8** (3.60 g, 82%) was recrystallized to give **8**, mp 189–190 °C. Anal. Calcd for $C_{27}H_{21}N_3O$: C, 80.37; H, 5.25; N, 10.41. Found: C, 80.43; H, 5.36; N, 10.17.

Rearrangement of 8 to 11-Oxo-*N,N'*-diphenyl-5(6*H*)-morphanthridinecarboxamidine (9). Compound **8** (1 g) was added to 35 mL of stirring, hot (170 °C) polyphosphoric acid. The reaction mixture was held at 150 °C for 1 h, cooled, and poured on 100 g of ice. The solution was extracted four times with 50-mL portions of $CHCl_3$. The $CHCl_3$ extracts were washed, dried ($MgSO_4$) and filtered. Evaporation of the $CHCl_3$ gave 0.95 g (95%) of crude **9** (mp 197–199 °C). Recrystallization from absolute ethanol gave yellow crystals melting at 202–203 °C. Anal. Calcd for $C_{27}H_{21}N_3O$: C, 80.37; H, 5.25; N, 10.41. Found: C, 80.37; H, 5.56; N, 9.96.

Reaction of 9 with *p*-Nitrobenzoyl Chloride. To a stirred suspension of 1 g (0.0025 mol) of **9** in 25 mL of Et_2O was added 0.303 g (0.003 mol) of Et_3N, followed by 0.463 g (0.0025 mol) of *p*-nitrobenzoyl chloride. The reaction mixture was stirred overnight and filtered. The Et_2O was evaporated and 25 mL of H_2O was added to the residue. After stirring for 3 min, the solution was filtered to give 1.25 g (92%) of the crude benzamido derivative (**9a**), melting at 210–213 °C. Purification of **9a** was accomplished by dissolving it in a minimum of hot 2-propanol and adding to the hot solution 5 mL of petroleum ether (bp 65–110 °C). Pure **9a** melted at 224–225 °C; molecular ion *m/e* 552. Anal. Calcd for $C_{34}H_{24}N_4O_4$: C, 73.88; H, 4.37; N, 10.13. Found: C, 73.99; H, 4.86; N, 9.68.

Thermolysis of 8. A solution of 0.50 g (0.0012 mol) of **8** in 10 mL of decalin was refluxed for 12 h. The reaction mixture was cooled in an ice bath and filtered to give 0.21 g (83%) of **10**. Compound **10** (mp 153–154 °C) was identified by comparison of IR spectra of an authentic sample and mass spectrometry. To the stirred filtrate was added 0.275 g (0.0012 mol) of picric acid. The reaction mixture was boiled briefly and the decalin evaporated to give 0.410 g (78%) of **12**. Recrystallization from 2-propanol gave **12** melting at 214–215 °C (lit. 213–214 °C).[4]

Acid Methanolysis of 6. A mixture of 0.500 g (0.0012 mol) of **6**, 15 mL of MeOH, and 10 drops of concentrated hydrochloric acid was refluxed for 3 h and then neutralized with a dilute sodium hydroxide solution. Filtration of the reaction mixture gave 0.500 g (92%) of **13**. Following recrystallization from methanol, **13** melted at 148–149.5 °C (molecular ion, *m/e* 449). Anal. Calcd for $C_{28}H_{23}N_3O_3$: C, 74.82; H, 5.16; N, 9.35. Found: C, 74.53; H, 5.45; N, 9.51.

Alternate Synthesis of 13. To a solution of 3.07 g (0.011 mol) of 1,2,3-triphenylguanidine and 1.12 g (0.012 mol) of Et_3N in 300 mL of Et_2O was added with stirring a solution of 2.2 g (0.011 mol) of *o*-carbomethoxybenzoyl chloride in 20 mL of Et_2O. The mixture was stirred for 3 h, followed by the addition of CH_2Cl_2. The reaction mixture was washed with H_2O and the Et_2O–CH_2Cl_2 layer dried ($MgSO_4$) and filtered. Evaporation of the solvents gave 3.13 g (65%) of crude **13**. A melting point of 148–150 °C was obtained

when 13 was recrystallized from methanol.

Thermolysis of 6. A solution of 0.500 g of 6 in 25 mL of decalin was refluxed for 132 h. The decalin was evaporated and the residue slurried well in 15 mL of Et_2O and filtered. The crude *N*-phenylphthalimide (0.150 g, 56%) melted at 195 °C and was recrystallized from MeOH to give material melting at 202–203 °C. The ether was evaporated and an IR spectrum of the residue was obtained. It showed the peaks common to *N*-phenylphthalimide and also an absorption band of high intensity at 2150 cm^{-1} which is characteristic for a carbodiimide.

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Registry No. 1a, 66730-24-3; **1b**, 71382-62-2; **1c**, 71382-63-3; **1d**, 71382-64-4; **2b**, 71382-65-5; **2d**, 71382-66-6; **3a**, 71382-67-7; **3b**, 71382-68-8; **3d**, 71382-69-9; **4**, 71382-70-2; **5**, 71382-71-3; **6**, 71382-72-4; **7**, 71382-73-5; **8**, 71382-74-6; **9**, 71382-75-7; **9a**, 71382-76-8; **10**, 5388-42-1; **11**, 622-16-2; **12**, 71382-77-9; **13**, 71382-78-0; *N,N'*-bis(4-bromophenyl)acetamidine, 71382-79-1; *o*-phthaloyl chloride, 88-95-9; *N,N'*-bis(4-ethoxyphenyl)acetamidine, 101-93-9; *N,N'*-diphenyl-α-phenylacetamidine, 19376-79-5; succinyl chloride, 543-20-4; furan-3,4-dicarboxylic acid, 3387-26-6; furan-3,4-dicarbonyl chloride, 52762-41-1; *N,N'*-diphenylacetamidine, 621-09-0; 2,5-dimethyl-1-phenylpyrrole-3,4-dicarboxylic acid, 52175-96-9; 2,5-dimethyl-1-phenylpyrrole-3,4-dicarbonyl chloride, 71411-04-6; 1,2,3-triphenylguanidine, 101-01-9; *o*-chloromethylbenzoyl chloride, 42908-86-1; *p*-nitrobenzoyl chloride, 122-04-3; decalin, 91-17-8; picric acid, 88-89-1; *o*-carbomethoxybenzoyl chloride, 4397-55-1; *N*-phenylphthalimide, 520-03-6.

Chemistry of Ethenesulfonyl Fluoride. Fluorosulfonylethylation of Organic Compounds[1]

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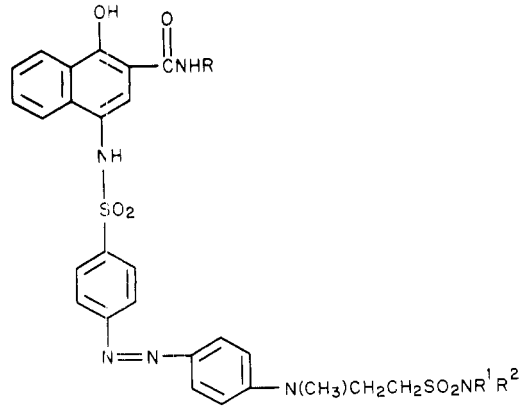
Ethenesulfonyl fluoride (ESF), a stable compound that is readily available from commercial isethionic acid (2-hydroxyethanesulfonic acid) or 2-chloroethanesulfonyl chloride, was shown to be a highly reactive yet selective and versatile intermediate in the synthesis of a wide variety of organosulfur compounds. ESF reacted with active methylene compounds, amines, sulfinates, and thiols to afford 2-fluorosulfonylethyl derivatives in generally excellent yields. The fluorosulfonyl group was stable to most reaction conditions but could be converted by simple, one-step procedures to sulfonamides, sulfonylimidazolides, and sulfonates and to sulfonic acids. ESF reacted with 2-aminoheterocyclic compounds such as 2-aminopyridine to produce fused 1,2,4-thiadiazine 1,1-dioxides, and it reacted with simple enamines to give 2-aminocyclobutanesulfonyl fluorides. Excellent yields resulted from alkylation of 3-amino-2-butenoates with ESF. Both classes of enamine products could be hydrolyzed to give fluorosulfonylated aliphatic and alicyclic ketones and aldehydes. ESF underwent cycloaddition to 2-methoxyfuran to yield 1-methoxy-6-(fluorosulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene, which was hydrolyzed to 2-(fluorosulfonyl)phenol in water. The general utility of ESF in synthesis was demonstrated by its application in the preparation of over 100 otherwise difficultly accessible new compounds.

In the course of work on the design and synthesis of dyes, we required a general and versatile technique for modifying the aqueous solubility of azo dyes by introduction of side-chain sulfonamide groups. For example, introduction of the function $CH_2CH_2SO_2NR^1R^2$ (R^1, R^2 = H or alkyl) into compounds such as



R, R^1, R^2 = H or alkyl

was desired. Since structural modification, or "fine tuning", of this type is essential to many branches of organic chemistry (for example, pharmaceuticals, pesticides, herbicides, and dyes), our findings are presented here regarding the utility of fluorosulfonylethylation reactions of ethenesulfonyl fluoride (**1**, ESF) in this type of organic synthesis. The cycloaddition and heterocyclization chemistry of ESF are also described.

Michael addition of aromatic amines to ethenesulfonamides appeared initially to offer the most direct route to the compounds we sought. Unfortunately, we were unable

$$ArNHR + CH_2{=}CHSO_2NR^1R^2 \rightarrow Ar(R)NCH_2CH_2SO_2NR^1R^2$$

R, R^1, R^2 = H or alkyl

to reproduce the preparation of ethenesulfonamide[2] in sufficient purity and quantity for our purposes. Efforts to prepare sulfonamides from the more readily accessible β-anilinoethanesulfonic acids were also unsuccessful.

$$Ar(R)NCH_2CH_2SO_3H \not\rightarrow Ar(R)NCH_2CH_2SO_2NR^1R^2$$

Goldberg[3] described the stepwise reaction of aniline with 2-chloroethanesulfonyl chloride to give 2-anilinoethanesulfonanilide, but the method did not appear suitable for

$$C_6H_5NH_2 + ClCH_2CH_2SO_2Cl \rightarrow [CH_2{=}CHSO_2NHC_6H_5] \rightarrow C_6H_5NHCH_2CH_2SO_2NHC_6H_5$$

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