The Preparation and Some Reactions of 2-(Arylsulfonyl)vinamidinium Salts

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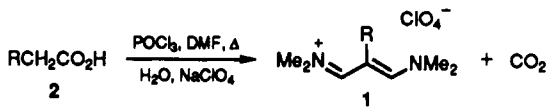
The preparation of novel 2-(arylsulfonyl)vinamidinium salts is described. The reactions of these materials with amidines, hydrazine, hydroxylamine, sodium borohydride, and Grignard reagents are presented along with an evaluation of their chemical behavior as compared to the 2-arylvinamidinium salts.

One of the primary goals of our research group over the last several years has been to uncover useful synthetic methodology related to the chemistry of vinamidinium salts[1] and their derivatives. The chemistry of vinamidinium salts has been reviewed,[1] and they have the potential of serving as three-carbon building blocks in the organic synthesis. Positions 1 and 3 of the vinamidinium system are electrophilic, and position 2 is weakly nucleophilic. One of the useful attributes of many vinamidinium salts (1) is their ease of preparation from substituted acetic acids (2) under Vilsmier-Haack conditions[2] (Scheme I).

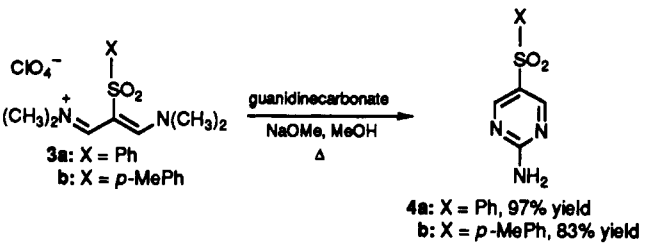
The parent compound (1, R = H) is available by a slightly diffrent and a more tedious procedure,[3] and the bulk of our work has focused primarily on the 2-arylvinamidinium system which is easily obtained by the method depicted in Scheme I. The nature of the R group appears to be rather important in determining whether the $POCl_3$/DMF conditions are successful. If one examines the literature for preparing 2-substituted vinamidinium salts[1,2] from an α-substituted acetic acid, a trend emerges that suggests successful C-2 substituents are aryl groups or electron-withdrawing groups (CN, NO_2, Cl, Br, CO_2R). This trend may be due to a ketene being generated from an α-substituted acetyl chloride intermediate.

The synthetic methods that we have developed[4] using 2-arylvinamidinium salts suggest that the aryl group at the 2-position of the vinamidinium salt has a pronounced effect on the reaction pathway observed. In order to understand and expand the general utility of vinamidinium salts as three-carbon building blocks in organic synthesis, it would be desirable to replace the 2-aryl group by a substituent that would (1) be compatable with α-substituted acetic acid synthesis, (2) offer the possibility of further functionalization or removal, and (3) allow for further studies on the effect of the 2-substituent on vinamidinium salt reactions. A group that seems to fit this criteria is the phenylsulfonyl moiety. This particular group has attracted significant, recent attention by Padwa,[5] Trost,[6] and others, and Magnus[7] has reviewed the relevant literature prior to 1977.

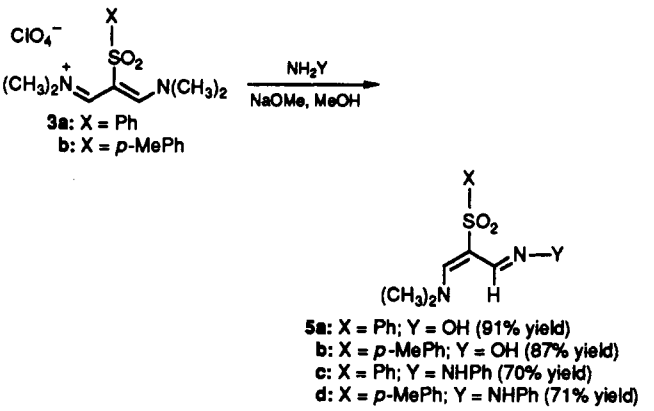
Scheme I



Scheme II



Scheme III



Trost has referred to this group as a "chemical chameleon" since a diverse group of reactions are possible. In addition, the phenylsulfonyl group has a long history[8] of being part of many pharmacologically active substances. The subsequent section describes the preparation and some reactions of 2-(arylsulfonyl)vinamidinium salts and a comparison to the chemistry previously observed for the 2-aryl systems.

Results and Discussion

In order to prepare a 2-(arylsulfonyl)vinamidinium salt it was first necessary to prepare the requisite 2-(arylsulfonyl)acetic acid. (Phenylsulfonyl)acetic acid is known[9] and is easily prepared by the reaction of the sodium salt of benzenesulfinic acid and α-bromoacetic acid in refluxing acetonitrile. Both the (phenylsulfonyl)- and ((*p*-methyl-

(1) For a review of the chemistry of vinamidinium salts, see: Lloyd, D.; NcNab, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 459. For recent related work by our research group, see also: Gupton, J.; Zembower, D.; Miller, J. *Synth. Commun.* **1988**, *18*, 1891. Gupton, J.; Layman, J. *J. Org. Chem.* **1987**, *52*, 3683. Gupton, J. *Aldrichimica Acta* **1986**, *19*, 43. Gupton, J.; Coury, J.; Moebus, M.; Fitzwater, S. *Synth. Commun.* **1986**, *16*, 1575. Gupton, J.; Norman, B.; Wysong, E. *Synth. Commun.* **1985**, *15*, 1305.

(2) Jutz, C. *Topics in Current Chemistry*; Springer-Verlag: New York, 1978; Vol. 73.

(3) Nair, V.; Cooper, C. *J. Org. Chem.* **1981**, *46*, 4759 and references therein.

(4) Gupton, J.; Andrew, S.; Lizzi, M. *Synth. Commun.* **1982**, *12*, 361. Gupton, J.; Polaski, C. *Ibid.* **1981**, *11*, 561. Gupton, J.; Colon, C. *Ibid.* **1984**, *14*, 271. Gupton, J.; Norman, B.; Wysong, E. *Ibid.* **1985**, *15*, 1305.

(5) (a) Padwa, A.; Kline, D.; Norman, B. *Tetrahedron Let.* **1988**, *29*, 265. (b) Padwa, A.; Norman, B. *Ibid.* **1988**, *29*, 2417. (c) Padwa, A.; Yeski, P. *J. Am. Chem. Soc.* **1988**, *110*, 1617.

(6) (a) Trost, B.; Ghadiri, M. *J. Am. Chem. Soc.* **1984**, *106*, 7260. (b) Trost, B.; Ghadiri, M. *Ibid.* **1986**, *108*, 1098. (c) Trost, B.; Lynch, J.; Renaut, P.; Steinman, D. *Ibid.* **1986**, *108*, 284.

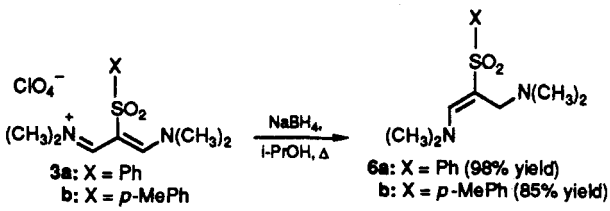
(7) Magnus, P. *Tetrahedron* **1977**, *33*, 2019.

(8) Csaky, T.; Barnes, B. *Cutting's Handbook of Pharmacology*, 7th *ed.*; Appleton-Centruy-Crafts: Norwalk, CT, 1984; pp 1-10.

(9) Cope, A. C.; Morrison, D. E.; Field, L. *J. Am. Chem. Soc.* **1950**, *72*, 59.

0022-3263/91/1956-0976$02.50/0

Scheme IV



phenyl)sulfonyl)acetic acids were prepared by this procedure. The (arylsulfonyl)acetic acids were then reacted with phosphorus oxychloride and DMF at 90–100 °C until carbon dioxide evolution ceased (approximately 3 h on a 0.015-mol scale). A 60–70% yield of the 2-(arylsulfonyl)vinamidinium salts (**3a** and **3b**) was obtained. With the desired salts in hand, we condensed the material with guanidine in methanol containing sodium methoxide (Scheme II).

Although the preparation of pyrimidines from vinamidinium salts is a well-known process,[1] this reaction is noteworthy in that a phenylsulfonylated heterocycle is produced and the vinamidinium salt has served as the vehicle for the incorporation of this group. Other dinucleophiles which are known[1] to react with vinamidinium salts are hydroxyl amine and hydrazines, and these are known to produce oxazoles and pyrazoles, respectively. Analogous reactions were carried out on the 2-(arylsulfonyl)vinamidinium salts, and these results are depicted in Scheme III.

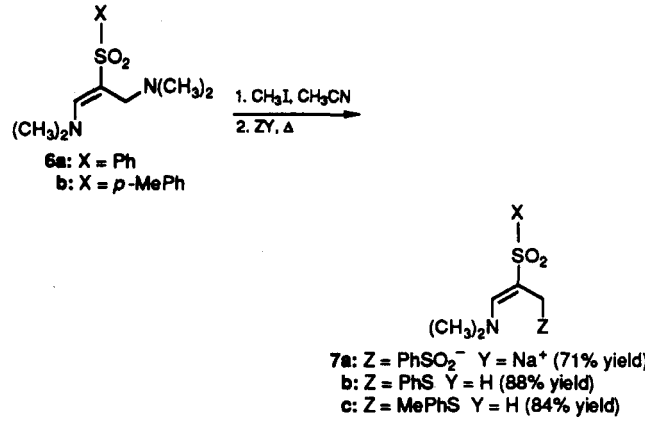
Hydroxylamine and phenylhydrazine did not react in the anticipated fashion but instead formed the acyclic oximes and hydrazones, respectively. This atypical behavior may be due to the arylsulfonyl group since such heterocycle preparations are well documented[1] for alkyl- and arylvinamidinium salts. This behavior may be the result of the "push–pull" relationship between the phenylsulfonyl and enamine groups, thereby allowing the imino group to behave like an "isolated" moiety. These compounds represent an interesting class of "vinylogous" sulfonamides and may possess useful synthetic transformations in their own right.

We have previously shown[4] that 2-arylvinamidinium salts react with sodium borohydride in refluxing 2-propanol to give 2-aryl-3-(dimethylamino)-1-propenes in good yield. We have suggested an amino enamine as an intermediate for such reactions, but it has never been isolated which may be due to the propensity of such species to undergo conjugate elimination followed by reduction. When the 2-(arylsulfonyl)vinamidinium salts were subjected to the standard reduction conditions, the respective (arylsulfonyl)amino enamines were isolated in good yield as well defined solids.

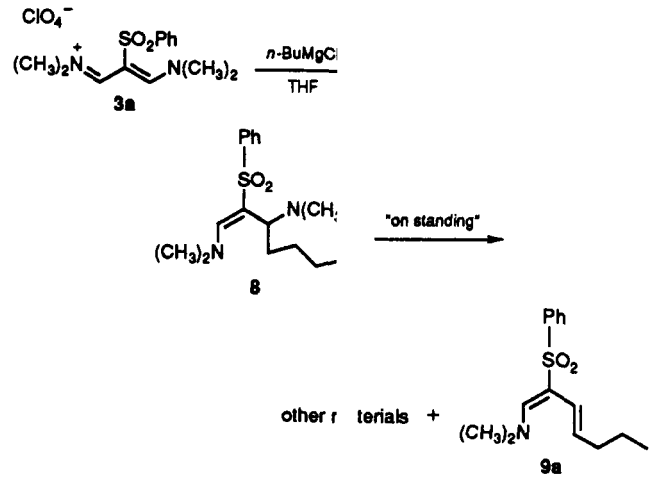
This result, therefore, seems to substantiate the earlier proposed[4] mechanism as well as to further support the lack of interaction of the enamine group with functionality at the 3-position of the propene. Again the "push–pull" nature of the vinylogous sulfonamide may be playing a significant role in such processes. These amino enamines appeared to be a rather interesting class of substances, and we decided to briefly examine their reactivity toward sulfur nucleophiles after initial reaction with iodomethane. Our intent was to see if the resultant quaternary ammonium group could be displaced, which would allow for further functionalizaton of this amino enamine.

All reactions worked reasonably well, and this suggests that a variety of nucleophilic displacements might be possible for further elaboration of this vinylogous sulfonamide. Another aspect of vinamidinium salt chemistry

Scheme V



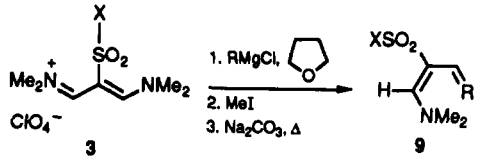
Scheme VI



that has been of some interest to us is the reaction with Grignard and organolithium reagents.[4] We have found that such reactions proceed in a clean fashion to afford 2,3-disubstituted α,β-unsaturated aldehydes after an acid workup. In light of the results obtained from previously described reactions of the (arylsulfonyl)vinamidinium salts, we subsequently examined this analogous reaction with organometallic species. In the first reaction studied with *n*-butylmagnesium chloride, the initially formed adduct appeared to be consistent with our notion of an amino enamine intermediate as depicted in Scheme VI.

However, on standing the crude product was slowly converted to several materials of which a sulfonylated amino diene appeared to be formed to the greatest extent. We felt that if this reaction could be optimized at the expense of other side reactions, this could prove to be useful synthetic methodology. Consequently, the crude reaction mixture was treated with iodomethane and anhydrous sodium carbonate to allow for quaternization and elimination of the Grignard–vinamidinium salt adduct. The resulting reaction product was free of impurities and was obtained in high yield. A number of analogous examples were studied, and these are reported in Table I. We believe the stereochemistry about both double bonds of the diene is trans since the vinyl hydrogens of the 3,4-double bond have ^1H coupling constants in the range of 17 Hz. The ^1H absorption of the dimethylamino groups appears as a singlet, and this suggests a trans relationship with the phenylsulfonyl moiety. That is, if the two groups were cis, one would expect to see nonequivalence of the two aminomethyl groups. Such reactions appear to be rather general for a variety of Grignard reagents which

Table I. Reaction of 2-(Arylsulfonyl)vinamidinium Salts (3) with Grignard Reagents



3 9

compd	X	R	% yield[a]
9a	Ph	*n*-butyl	88
9b	Ph	*n*-octyl	90
9c	Ph	*n*-pentyl	98
9d	Ph	ethyl	97
9e	Ph	isopropyl	92
9f	*p*-MePh	ethyl	94
9g	*p*-MePh	isopropyl	92
9h	*p*-MePh	*n*-butyl	88
9i	*p*-MePh	*n*-pentyl	92
9j	*p*-MePh	*n*-octyl	94

[a] All reported yields refer to products which have been recrystallized from hexane/THF.

includes the more sterically incumbered members such as isopropyl. These 1-amino-2-(arylsulfonyl) 1,3-dienes may possess interesting chemical reactions, and appropriate studies are now underway in our laboratory.

In summary, 2-(arylsulfonyl)vinamidinium salts can be prepared from the corresponding 2-(arylsulfonyl)acetic acids in good yield. These vinamidinium salts react cleanly with a variety of nucleophiles, reducing and organometallic reagents to produce substances that incorporate the arylsulfonyl group. Such reactions also help to clarify the effect of the 2-substituent on vinamidinium salt reactivity and further substantiate the utility of such substances as three-carbon building blocks in organic synthesis.

Experimental Section[10]

[(4-Methylphenyl)sulfonyl]acetic Acid (2). This compound was prepared in a manner identical with that of (phenylsulfonyl)acetic acid[9] with the exception that the sodium salt of 4-methylbenzenesulfonic acid was used. The product was obtained in 59% yield after recrystallization from methylene chloride and exhibited the following properties: mp 111–113 °C; ^{1}H NMR (DMSO-d_6) δ 2.42 (s, 3 H), 4.42 (s, 2 H), 7.42 (d, J = 7 Hz, 2 H), and 7.80 (d, J = 7 Hz, 2 H); ^{13}C (DMSO-d_6) δ 21.03, 60.19, 128.32, 129.92, 136.69, 144.89, and 164.42: IR (Nujol) 1720, 1320, and 1140 cm^{-1}; mass spectrum, m/z 214 (EI, M$^+$). Anal. Calcd for $C_9H_{10}O_4S$: C, 50.69; H, 4.26. Found: C, 48.98; H, 4.64.

2-(Phenylsulfonyl)-1,1,5,5-tetramethyl-1,5-diazapentadienium Perchlorate (3a). A mixture of DMF (7 mL), phosphorus oxychloride (6.9 g, 0.045 mol), and (phenylsulfonyl)acetic acid (3.0 g, 0.015 mol) was heated at 90 °C for 3 h, during which time carbon dioxide was evolved. The reaction mixture was cooled in an ice–water bath and poured into 50 mL of ice–water containing 3.2 g (0.026 mol) of sodium perchlorate. The mixture was cooled in an ice bath, and the resulting yellow solid (3.4 g, 62% yield) was filtered and dried under vacuum: mp 180–183 °C; ^{1}H NMR (DMSO-d_6) δ 2.98 (s, 6 H), 3.55 (s, 6 H), 7.62 (m, 3 H), 7.92 (d, J = 7.5 Hz, 2 H), and 8.45 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 42.6, 47.8, 98.9, 126.3, 129.9, 133.3, 143.9, and 162.6; IR (Nujol 1630, 1375, 1140, and 815 cm^{-1}. Anal. Calcd for $C_{13}H_{19}N_2O_6ClS$: C, 42.56; H, 5.23; N, 7.64; S, 8.74. Found: C, 42.29; H, 4.97; N, 7.38; S, 8.76.

2-[(4-Methylphenyl)sulfonyl]-1,1,5,5-tetramethyl-1,5-diazapentadienium Perchlorate (3b). This compound was prepared in 62% yield in a manner identical with the previous procedure from [(4-methylphenyl)sulfonyl]acetic acid: mp 160–163 °C; ^{1}H NMR (DMSO-d_6) δ 2.38 (s, 3 H), 2.95 (s, 6 H), 3.55 (s, 6 H), 7.40 (d, J = 7 Hz, 2 H), 7.80 (d, J = 7 Hz, 2 H), and 8.42 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 20.96, 42.59, 47.71, 99.39, 126.42, 130.27, 141.15, 143.76, and 162.49; IR (Nujol) 1630, 1375, and 1140 cm^{-1}. Anal. Calcd for $C_{14}H_{21}ClN_2O_6S$: C, 44.15; H, 5.57; N, 7.36; S, 8.42. Found: C, 44.42; H, 5.28; N, 7.24; S, 8.59.

2-Amino-5-(phenylsulfonyl)pyrimidine (4a). A dispersion of 60% sodium hydride (0.7 g, 0.018 mol) in mineral oil was washed with 10 mL of hexane, absolute methanol (50 mL) was added, and the mixture was allowed to react for several minutes. The mixture was cooled to room temperature, and 1.5 g (0.0083 mol) of guanidinecarbonate and 3.0 g (0.0082 mol) of the 2-(phenylsulfonyl)vinamidinium salt were added to the reaction vessel. The mixture was refluxed for 4 h and cooled to room temperature. The solvent was removed in vacuo, and a small amount of water was added to the residue. The resulting solid was filtered and dried in vacuo to yield 1.87 g (97% yield) of a solid: mp 191–195 °C; ^{1}H NMR ($CDCl_3$) δ 7.38 (br s, 2 H), 7.60 (m, 3 H), 7.92 (d, J = 5 Hz, 2 H), and 8.68 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 123.85, 126.74, 129.46, 133.23, 142.12, 158.25, and 164.79; IR (Nujol) 3300, 3150, 1660, 1375, 1160, 1130 cm^{-1}; mass spectrum, m/z 235 (EI, M$^+$). Anal. Calcd for $C_{10}H_9N_3O_2S$: C, 51.06; H, 3.86; N, 17.86. Found: C, 50.71; H, 3.74; N; 17.72.

2-Amino-5-[(4-methylphenyl)sulfonyl]pyrimidine (4b). This compound was prepared in 83% yield in a manner identical with the preparation of 2-amino-5-(phenylsulfonyl)pyrimidine (**4a**): mp 210–212 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 8.24 (br s, 2 H), 7.33 (d, J = 7 Hz, 2 H), 7.80 (d, J = 7 Hz, 2 H), and 8.70 (s, 2 H); ^{13}C NMR (DMSO-d_6) 21.02, 123.93, 127.13, 130.48, 139.61, 144.40, 158.66, and 164.89; IR (Nujol) 3275, 3150, 1660, 1370, 1150 and 1125 cm^{-1}; mass spectrum, m/z 249 (EI, M$^+$). Anal. Calcd for $C_{11}H_{11}N_3O_2S$: C, 52.99; H, 4.46; N, 16.86. Found: C, 53.23; H, 4.31; N, 16.68.

3-(Dimethylamino)-2-(phenylsulfonyl)propenal Oxime (5a). This compound was prepared by a method analogous to that used for 2-amino-5-(phenylsulfonyl)pyrimidine (**4a**) with the exception that after removing the solvent in vacuo from the reaction mixture, the residue was partitioned between water and chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate, and the filtrate was concentrated in vacuo to give an 81% yield of the oxime after recrystallization from methanol/water: mp 124–128 °C; ^{1}H NMR (DMSO-d_6) δ 3.00 (s, 6 H), 7.40–7.60 (m, 4 H), and 7.72–7.82 (m, 3 H); ^{13}C NMR ($CDCl_3$/Cl_3CCO_2H) δ 35.93, 125.88, 127.82, 130.33, 134.93, 141.04, 147.46, and 161.38; IR (Nujol) 3330, 1620, 1290, and 1160 cm^{-1}; mass spectrum, m/z 254 (EI, M$^+$). Anal. Calcd for $C_{11}H_{14}N_2O_3S$: C, 51.94; H, 5.56; N, 11.02. Found: C, 51.96; H, 5.28; N, 10.80.

3-(Dimethylamino)-2-[(4-methylphenyl)sulfonyl]propenal Oxime (5b). This compound was prepared by a method analogous to that used for 2-amino-5-(phenylsulfonyl)pyrimidine (**4a**): mp 177–182 °C; ^{1}H NMR (DMSO-d_6) δ 2.30 (s, 3 H), 2.98 (s, 6 H), 7.28 (d, J = 9 Hz, 2 H), 7.45 (s, 1 H), 7.62 (d, J = 9 Hz, 2 H), and 7.75 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 20.91, 43.78, 98.31, 126.73, 129.66, 141.27, 141.71, 142.41, and 149.50; IR (Nujol) 3240, 1615, 1270, and 1130 cm^{-1}; mass spectrum, m/z 269 (FAB, M$^+$ + H). Anal. Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.71; H, 6.02. Found: C, 54.37; H, 5.05.

3-(Dimethylamino)-2-(phenylsulfonyl)propenal Phenylhydrazone (5c). This compound was prepared by a method analogous to that used for 2-amino-5-(phenylsulfonyl)pyrimidine (**4a**). A 70% yield of the hydrazone was obtained, and the crude product was recrystallized from a 90/10 methanol/water mixture: mp 178–181 °C; ^{1}H NMR ($CDCl_3$) δ 3.20 (s, 6 H), 6.72 (t, J = 9 Hz, 1 H), 6.82 (d, J = 9 Hz, 2 H), 7.14 (t, J = 9 Hz, 2 H), 7.43 (s, 1 H), 7.50 (m, 3 H), 7.72 (s, 1 H), and 7.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 44.76, 102.34, 112.83, 119.89, 127.19, 129.35, 129.67, 130.93, 132.36, 144.13, 145.27, and 148.69; IR ($CHCl_3$) 3300, 1620, 1285, 1140 cm^{-1}; mass spectrum, m/z 329 (EI, M$^+$). Anal. Calcd for $C_{17}H_{18}N_3SO_2$: C, 62.16; H, 5.54; N, 12.80. Found: C, 61.98; H, 5.83; N, 12.78.

3-(Dimethylamino)-2-[(4-methylphenyl)sulfonyl]propenal Phenylhydrazone (5d). This compound was prepared by a method analogous to that used for 2-amino-5-(phenylsulfonyl)-pyrimidine (**4a**): mp 177–182 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 3.03 (s, 6 H), 6.62 (t, J = 8 Hz, 1 H), 6.73 (d, J = 8 Hz, 2 H), 7.10 (t, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 7.40 (s, 1 H), 7.65 (m, 3 H); ^{13}C NMR (DMSO-d_6) δ 20.93, 44.08, 102.07, 111.80,

(10) All yields reported herein refer to crude products unless otherwise specified.

118.21, 126.79, 129.35, 129.69, 130.79, 141.59, 142.40, 145.84, and 148.04; IR (Nujol) 3200, 1620, 1260, and 1145 cm^{-1}; mass spectrum, m/z 343 (EI, M^+). Anal. Calcd for $C_{18}H_{21}N_3O_2S$: C, 62.94; H, 6.18; N, 12.24. Found: C, 62.86; H, 5.96; N, 12.10.

1,3-Bis(dimethylamino)-2-(phenylsulfonyl)-1-propene (6a). A mixture of 2.00 g of sodium borohydride (0.053 mol) and 300 mL of 2-propanol was stirred for 5 min under nitrogen, and 5 g of the 2-(phenylsulfonyl)vinamidinium salt (**3a**) was added. The mixture was refluxed for 22h, the solvent was removed in vacuo, and the residue was partitioned between water and chloroform. The chloroform layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to yield 3.58 g of product (98% yield). This material can be further purified by recrystallization from THF/hexane if desired: mp 85 °C; ^1H NMR ($CDCl_3$) δ 2.05 (br s, 6 H), 3.01 (br s, 2 H), 3.18 (br s, 6 H), 7.45 (m, 4 H), and 7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 42.91, 44.18, 53.55, 100.23, 127.45, 129.16, 131.99, 144.73, and 150.55; IR ($CHCl_3$) 1610, 1280, 1140, and 815 cm^{-1}; mass spectrum, m/z 268 (EI, M^+). Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 58.17; H, 7.53; N, 10.44. Found: C, 58.13; H, 7.33; N, 10.36.

1,3-Bis(dimethylamino)-2-[(4-methylphenyl)sulfonyl]-1-propene (6b). This compound was prepared in 85% yield by a method identical to the previous procedure with the exception that the [(4-methylphenyl)sulfonyl]vinamidinium perchlorate (**3b**) was used instead of the (phenylsulfonyl)vinamidinium salt: mp 106–108 °C; ^1H NMR ($CDCl_3$) δ 2.02 (s, 6 H), 2.38 (s, 3 H), 2.98 (s, 2 H), 3.12 (s, 6 H), 7.20 (d, J = 7.2 Hz, 2 H), 7.42 (s, 1 H), and 7.67 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.49, 42.79, 44.11, 53.22, 100.61, 127.38, 129.61, 141.74, 142.37, and 150.47; IR ($CHCl_3$) 1630, 1280, and 1140 cm^{-1}; mass spectrum, m/z 282 (EI, M^+). Anal. Calcd for $C_{14}H_{20}N_2O_2S$: C, 59.96; H, 7.20. Found: C, 59.68; H, 7.14.

Preparation of 1-(Dimethylamino)-2,3-bis(phenylsulfonyl)-1-propene (7a). A mixture of 1.00 g (0.00373 mol) of 1,3-bis(dimethylamino)-2-(phenylsulfonyl)-1-propene (**6a**), 0.80 g (0.00563 mol) of iodomethane, and 15 mL of dry acetonitrile was stirred for 30 min, and 1.20 g (0.00732 mol) of benzenesulfinic acid sodium salt was added. The resulting mixture was refluxed with stirring for 8 h, and the solvent was removed in vacuo. The residue was partitioned between chloroform (50 mL) and water (50 mL), and after additional chloroform extractions the combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to yield 1.18 g of semisolid. A portion (0.525 g) of the semisolid was subjected to radial chromatography using a Harrison chromatotron and a 50:50 mixture of ethyl acetate/hexane as the eluant to give 0.428 g (71% yield) of a solid: mp 122–123 °C; ^1H NMR ($CDCl_3$) δ 3.15 (br s, 6 H), 4.32 (br s, 2 H), and 7.35–7.85 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 30.88, 42.94, 98.81, 126.80, 127.83, 129.23, 129.39, 129.83, 132.46, 137.32, 143.91, and 149.59; IR ($CHCl_3$) 3000 and 1620 cm^{-1}; mass spectrum, m/z 366 (CI, M^+); HRMS (CI) for $C_{17}H_{19}NO_4S_2$ calcd 366.0834, found 366.0831. Anal. Calcd for $C_{17}H_{19}NO_4S_2$: C, 55.86; H, 5.25; N, 3.83. Found: C, 54.94; H, 4.91; N, 3.60.

1-(Dimethylamino)-2-(phenylsulfonyl)-3-(phenylthio)-1-propene (7b). This compound was prepared in 88% yield by a method analogous to compound **7a**: mp 114–115 °C; ^1H NMR ($CDCl_3$) δ 3.1 (br s, 6 H), 4.0 (br s, 2 H), 7.20 (m, 5 H), 7.45 (m, 4 H), and 7.85 (m, 2 H); ^{13}C NMR δ 30.88, 42.94, 98.45, 126.8, 127.82, 129.23, 129.39, 129.83, 132.46, 137.32, 143.91, and 149.59; IR ($CHCl_3$) 3000 and 1620 cm^{-1}; mass spectrum, m/z 334 (CI, M^+). Anal. Calcd for $C_{17}H_{19}NO_2S_2$: C, 61.22; H, 5.75; N, 4.24. Found: C, 60.98; H, 6.03; N, 4.12.

1-(Dimethylamino)-2-(phenylsulfonyl)-3-[(4-methylphenyl)thio]-1-propene (7c). This compound was prepared in 84% yield by a method analogous to compound **7a**: mp 109–112 °C; ^1H NMR ($CDCl_3$) δ 2.22 (br s, 3 H), 3.05 (br s, 6 H), 3.92 (br s, 2 H), 7.05 (m, 4 H), 7.45 (m, 4 H), and 7.85 (m, 2 H); ^{13}C NMR δ 21.26, 31.65, 42.95, 48.60, 127.75, 129.29, 130.22, 130.69, 132.5, 133.5, 137.09, 143.99, and 149.66; IR ($CHCl_3$) 3000 and 1620 cm^{-1}; mass spectrum, m/z 348 (CI, M^+); HRMS (CI) for $C_{18}N_{21}NO_2S_2$ calcd 348.1092, found 348.1089. Anal. Calcd for $C_{18}H_{21}NO_2S_2$: C, 62.20; H, 6.10; N, 4.03. Found: C, 61.25; 5.71; N, 3.34.

Reaction of 2-(Phenylsulfonyl)-1,1,5,5-tetramethyl-1,5-diazapentadienium Perchlorate with Ethylmagnesium Chloride (9d). A mixture of 2 g of the 2-(phenylsulfonyl)vinamidinium salt (**3a**) and 150 mL of anhydrous THF under nitrogen was cooled to 0 °C, and 5.5 mL of 2 M ethylmagnesium chloride solution in THF was added. The reaction mixture, which became a light yellowish brown solution, was stirred at 0 °C for 1 h and then at 25 °C for 1 h. Methyl iodide (2.34 g, 0.0165 mol) was added, and the mixture was allowed to stir for 15 min. Subsequently, 1.75 g of anhydrous Na_2CO_3 (0.0165 mol) was added, and the reaction mixture was heated at reflux for 3 h. The mixture was cooled, and 30 mL of water was added. The THF was then removed in vacuo, and the residue was partitioned between water and chloroform. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo, to yield 1.41 g of crude material which upon recrystallization from a 90:10 mixture of hexane/THF yielded 1.30 g of a solid: mp 122–123 °C; ^1H NMR ($CDCl_3$) δ 1.59 (d, J = 7 Hz, 3 H), 2.88 (br s, 6 H), 5.46 (m, 1 H), 5.84 (d, J = 17 Hz, 1 H), 7.18 (s, 1 H), 7.35 (m, 3 H), and 7.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.62, 43.32, 104.06, 120.20, 127.39, 128.78, 131.95, 133.02, 143.20, and 146.82; IR ($CHCl_3$) 689, 717, 1138, 1275, 1395, 1620, 1644, and 2845 cm^{-1}; mass spectrum, m/z 251 (EI, M^+). Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.11; H, 6.83; N, 5.57. Found: C, 61.98; H, 6.60; N, 5.45.

(*E*)-1-(Dimethylamino)-2-(phenylsulfonyl)-4-methyl-1,3-pentadiene (9e). This material was prepared in 92% yield by a method analogous to the preparation of compound **9d**: mp 141–142 °C; ^1H NMR ($CDCl_3$) δ 1.0 (s, 3 H), 1.67 (s, 3 H), 2.83 (br s, 6 H), 5.65 (s, 1 H), 7.25 (s, 1 H), 7.4 (m, 3 H), and 7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.20, 24.92, 42.19, 103.83, 155.42, 127.74, 128.82, 131.94, 143.07, 144.02, and 146.72; IR ($CHCl_3$) 685, 715, 1135, 1280, 1390, 1620, 1640, and 2840 cm^{-1}; mass spectrum, m/z 265 (EI, M^+). Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.35; H, 7.23; N, 5.28. Found: C, 62.94; H, 7.27; N, 5.02.

(*E*,*E*)-1-(Dimethylamino)-2-(phenylsulfonyl)-1,3-heptadiene (9a). This material was prepared in 88% yield by a method analogous to the preparation of compound **9d**: mp 49–50 °C; ^1H NMR ($CDCl_3$) δ 0.72 (t, J = 7 Hz, 3 H), 1.23 (m, 2 H), 1.93 (q, J = 7 Hz, 2 H), 2.93 (br s, 6 H) 5.5 (m, 1 H), 5.87 (d, J = 17 Hz, 1 H), 7.22 (s, 1 H), 7.39 (m, 3 H), and 7.73 (m, 2 H); ^{13}C NMR δ 13.74, 22.48, 35.51, 43.49, 104.39, 119.39, 127.7, 128.86, 132.06, 138.39, 143.10, and 146.82; IR ($CHCl_3$) 688, 715, 1135, 1279, 1395, 1620, 1640, and 2860 cm^{-1}; mass spectrum m/z 279 (EI, M^+). Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.47; H, 7.59; N, 5.01. Found: C, 64.31; H, 7.57; N, 4.95.

(*E*,*E*)-1-(Dimethylamino)-2-(phenylsulfonyl)-1,3-octadiene (9c). This material was prepared in 98% yield by a method analogous to the preparation of compound **9d**: mp 52–53 °C; ^1H NMR ($CDCl_3$) δ 0.78 (t, J = 7 Hz, 3 H), 1.16 (m, 4 H), 1.95 (q, J = 7 Hz, 2H), 2.94 (br s, 6 H), 5.5 (m, 1 H), 5.89 (d, J = 17 Hz, 1 H), 7.28 (s, 1 H), 7.42 (m, 3 H), and 7.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.22, 31.45, 33.1, 43.51, 106.46, 119.23, 127.75, 128.85, 132.05, 138.69, 143.09, and 146.78; IR ($CHCl_3$) 695, 720, 1142, 1285, 1400, 1625, 1647, and 2860 cm^{-1}; mass spectrum, m/z 293 (EI, M^+). Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.48; H, 7.92; N, 4.77. Found: C, 65.27; H, 7.71; N, 4.51.

(*E*,*E*)-1-(Dimethylamino)-2-(phenylsulfonyl)-1,3-undecadiene (9b). This material was prepared in 90% yield by a method analogous to the preparation of compound **9d**: mp 50–51 °C; ^1H NMR ($CDCl_3$) δ 0.82 (t, J = 7 Hz, 3 H), 1.13 (br s, 10 H), 1.93 (q, J = 7 Hz, 2 H), 2.92 (br s, 6 H), 5.51 (m, 1 H), 5.87 (d, J = 17 Hz, 1 H), 7.24 (s, 1 H), 7.38 (m, 3 H), and 7.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.28, 22.84, 29.21, 29.34, 32.01, 33.44, 43.50, 104.42, 119.2, 127.73, 128.84, 132.05, 138.69, 143.72, and 146.80; IR ($CHCl_3$) 692, 720, 1140, 1280, 1400, 1625, and 2860 cm1–1; mass spectrum, m/z 335 (EI, M^+). Anal. Calcd for $C_{19}H_{29}NO_2S$: C, 68.00; H, 8.73; N, 4.18. Found: C, 68.29; H, 9.00; N, 3.88.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)sulfonyl]-1,3-pentadiene (9f). This material was prepared in 94% by a method analogous to the preparation of compound **9d**: mp 154–155 °C; ^1H NMR ($CDCl_3$) δ 1.60 (dd, J = 2 Hz, J = 7 Hz, 3 H), 2.30 (s, 3 H), 2.90 (s, 6 H), 5.50 (dq, J = 16 Hz, J = 7 Hz, 1 H), 5.88 (br d, J = 16 Hz, 1 H), 7.15 (d, J = 8 Hz, 2 H), and 7.60 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.79, 21.65, 43.45, 104.77, 120.40, 127.64, 129.55, 133.01, 144.47, 142.62, and 146.68; IR ($CHCl_3$) 1630, 1610, 1380, 1120, and 800 cm^{-1}; mass spectrum, m/z 265 (IE, M^+). Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.35; H, 7.23; N, 5.28. Found: C, 63.31; H, 7.41; N, 5.18.

(*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)sulfonyl]-4-methyl-1,3-pentadiene (9g). This material was prepared in 92%

yield by a method analogous to the preparation of compound **9d**: mp 141-142 °C; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.71 (s, 3 H), 2.39 (s, 3 H), 2.88 (s, 6 H), 5.68 (s, 1 H), 7.20 (d, J = 8 Hz, 2 H), 7.27 (s, 1 H), and 7.62 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.28, 21.64, 24.93, 42.16, 104.10, 115.47, 127.72, 129.42, 140.26, 142.46, 143.82, and 146.46; IR ($CHCl_3$) 1625, 1390, 1135, and 810 cm^{-1}; mass spectrum, m/z 279 (EI, M$^+$). Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.47; H, 7.59; N, 5.01. Found: C, 64.35; H, 7.72; N, 4.99.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)-sulfonyl]-1,3-heptadiene (9h). This material was prepared in 88% yield by a method analogous to the preparation of compound **9d**: mp 45-46 °C; ^{1}H NMR ($CDCl_3$) δ 0.71 (t, J = 7 Hz, 3 H), 1.22 (hex, J = 7 Hz, 2 H), 1.92 (q, J = 7 Hz, 2 H), 2.32 (s, 3 H), 2.91 (s, 6 H), 5.51 (dt, J = 16 Hz, J = 7 Hz, 1 H), 5.85 (d, J = 16 Hz, 1 H), 7.16 (d, J = 8 Hz, 2 H), 7.22 (s, 1 H), and 7.60 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.76, 21.63, 22.52, 35.56, 43.48, 104.82, 119.45, 127.76, 129.48, 138.18, 140.26, 142.62, and 146.58; IR ($CHCl_3$) 1625, 1400, and 1140 cm1-^{1}; mass spectrum, m/z 293 (EI, M$^+$). Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.48; H, 7.92; N, 4.77. Found: C, 65.62; H, 8.02; N, 4.65.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)-sulfonyl]-1,3-octadiene (9i). This material was prepared in 92% yield by a method analogous to the preparation of compound **9d**: mp 58-59 °C; ^{1}H NMR ($CDCl_3$) δ 0.77 (t, J = 7 Hz, 3 H), 1.15 (m, 4 H), 1.95 (q, J = 7 Hz, 2 H), 2.35 (s, 3 H), 2.93 (s, 6 H), 5.12 (dt, J = 16 Hz, J = 7 Hz, 1 H), 5.87 (d, J = 16 Hz, 1 H), 7.18 (d, J = 8 Hz, 2 H), 7.24 (s, 1 H), and 7.62 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.05, 21.64, 31.48, 33.14, 43.49, 104.84, 119.32, 127.79, 129.48, 138.41, 140,24, 142.61, and 146.54; IR ($CHCl_3$) 1630, 1400, and 1140 cm^{-1}; mass spectrum, m/z 307 (EI, M$^+$). Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.40; H, 8.21; N, 4.56. Found: C, 66.15; H, 8.22; N, 4.52.

(*E*,*E*)-1-(Dimethylamino)-2-[(4-methylphenyl)-sulfonyl]-1,3-undecadiene (9j). This material was prepared in 94% yield by a method analogous to the preparation of compound **9d**: mp 61-62 °C; ^{1}H NMR ($CDCl_3$) δ 1.82 (t, J = 7 Hz, 3 H), 1.15 (m, 10 H), 1.92 (q, J = 7 Hz, 2 H), 2.32 (s, 3 H), 2.92 (s, 6 H), 5.53 (dt, J = 16 Hz, J = 7 Hz, 1 H), 5.88 (d, J = 16 Hz, 1 H), 7.16 (d, J = 9 Hz, 2 H), 7.26 (s, 1 H), and 7.62 (d, J = 9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.29, 21.64, 22.87, 29.22, 29.36, 32.03, 33.47, 43.49, 104.85, 119.27, 127.79, 129.48, 138.42, 140.27, 142.58, and 146.55; IR ($CHCl_3$) 1630, 1405, and 1145 cm^{-1}; mass spectrum, m/z 349 (EI, M$^+$). Anal. Calcd for $C_{20}H_{31}NO_2S$: C, 68.71; H, 8.96; N, 4.01. Found: C, 69.00; H, 9.01; N, 3.95.

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New Synthesis of Pyrrolo[3,2,1-*ij*]quinolin-4-one Derivatives

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A new convenient synthesis of pyrrolo[3,2,1-*ij*]quinolin-4-one derivatives is described. In this method, methyl-7-hydroxyquinoline-2-ones are the starting materials onto which the third pyrrolo ring is condensed directly, yielding dehydrogenated methyl-9-hydroxypyrrolo[3,2,1-*ij*]quinolin-4-ones.

Introduction

The tricyclic 4*H*-pyrrolo[3,2,1-*ij*]quinoline system has been known for a long time. In fact, the so-called methyldiketolilolidine (i.e. 2-methyl-1,2,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinoline-4,6-dione) was first obtained by Knorr quinoline synthesis from 2-methylindoline.[1]

More recently, polyfluorohydroxyisopropyl derivatives of 1,2-dihydropyrrolo[3,2,1-*ij*]quinolin-4-one have been synthesized and tested for antihypertensive activity,[2] and 1,2,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolin-4-one and some analogues have been prepared as systemic fungicides of agricultural interest.[3a,b]

All previous synthetic pathways to obtain pyrroloquinolinones used indoline or its derivatives as the starting materials.[2,3a,4-7]

We now report a new, less expensive method for obtaining pyrrolo[3,2,1-*ij*]quinolin-4-one derivatives, which consists of building a pyrrole ring at the appropriate position of the quinolinone nucleus. In this way dehydrogenated methyl 9-hydroxy derivatives of the title tricyclic system may be directly synthesized. Useful intermediates are 8-allyl derivatives of 7-hydroxyquinolin-2-

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