

Synthesis of 1-Aryl-3,4-Dimethylenepyrrolidines by the Thermal Elimination of Sulfur Dioxide

Raphael M. Ottenbrite and Peter V. Alston

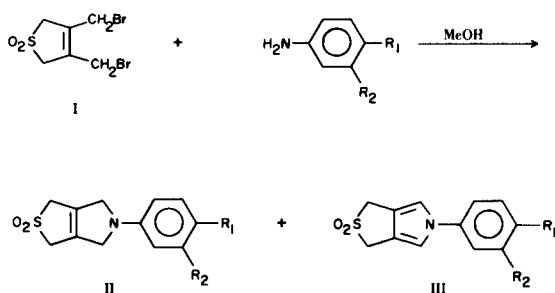
Department of Chemistry and Pharmaceutical Chemistry,
Virginia Commonwealth University, Richmond, Virginia 23298

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The reaction of 3,4-bis(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide with arylamines to produce 5-aryl-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxides was investigated. It was found that the bicyclic compound was obtained in good yields for arylamines with substituent groups with Hammett σ values of less than 0.40. These bicyclic compounds were thermally decomposed to produce the corresponding 1-aryl-3,4-dimethylenepyrrolidines in good yields. Several accompanying products of both of the above reactions were isolated and characterized.

Recently there has been considerable interest in regard to the synthesis of 3,4-dimethylenepyrrolidines (1-3). These compounds are of specific interest as reactants in the Diels-Alder reaction (3), as monomers in polymerization reactions and for their medicinal applications (4). We have earlier reported the general application (5) of the reaction of 3,4-bis(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide (I) with primary amines to produce 1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxides (II). In this paper we wish to present the optimization and the scope and limitations of this reaction with monosubstituted arylamines as well as the thermal decomposition of these bicyclic compounds (II) to produce the corresponding 1-aryl-3,4-dimethylenepyrrolidines (IV). Several other reaction products of both of these reactions have been also isolated and characterized.

In the reaction of monosubstituted arylamines with I, it was found that optimum yields were obtained by refluxing the reaction mixture in the presence of sodium carbonate for 1-4 hours depending on the nucleophilicity of the amine (Table I). The bicyclic product (II) was



$R_1 = H, R_2 = H, CH_3, OCH_3, Cl$
 $R_1 = H, R_2 = N(CH_3)_2, OCH_3, CH_3, Cl, COOEt$

obtained in good yields for arylamines with substituent groups having Hammett σ values of 0.40 or less (Tables I and II). It was found that when arylamines having substituents with σ values greater than 0.60 were similarly treated for 4 hours only starting material was recovered. Further, when the reaction time was increased to 24 hours, an intractable oil was obtained. It would appear that the nucleophilicity of the arylamine in this range is too weak to compete with an apparent 1,4-HBr elimination reaction. The oxidized compound (III) was observed in all reaction mixtures. It was only isolated, however, in two cases, 5-(*p*-methylphenyl)-1,3-dihydrothieno[3,4-*c*]pyrrole 2,2-dioxide and 5-phenyl-1,3-dihydrothieno[3,4-*c*]pyrrole 2,2-dioxide.

The 5-aryl-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxides (II) were decomposed readily upon heating, expelling sulfur dioxide to yield the corresponding exocyclic dienes (IV). This decomposition was carried out in a sublimator with the exocyclic diene and a small amount of the rearranged product, 1-substituted-3,4-dimethylpyrrole (V) being recovered. Most of the 1-aryl-3,4-dimethylenepyrrolidines (Table III) did not have a detectable melting point due to their fast rates of polymerization and dimerization at elevated temperatures. These compounds were found, however, to be stable for months when left in a refrigerator. Further studies are presently under way on the rearrangement of these 3,4-dimethylenepyrrolidines to their corresponding pyrrole isomer (V). The remaining products (residue in the sublimator) which did not sublime at the decomposition temperatures were found to be a mixture of the corresponding dimer and trimer. The dimer (VI) was isolated by sublimation of the mixture at 200° under reduced pressure.

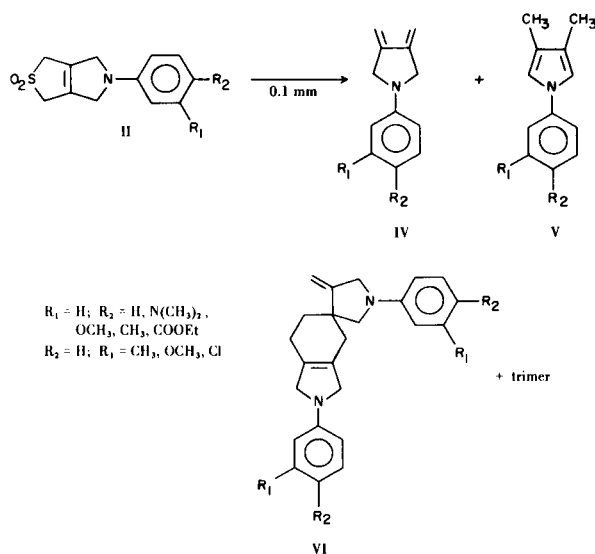
TABLE I

Reaction of Monosubstituted Arylamines with 3,4-Bis(bromomethyl)-2,5-dihydrothiophene 1,1-Dioxide to form Compounds of Type II.

Arylamine	Substrate pKa (c)	Substituent σ (d)	Reaction Time (hrs.)	% Yield
<i>p</i> - <i>N,N</i> -Dimethylphenylenediamine	-----	-.83	3	50
<i>p</i> -Anisidine	5.34	-.27	2	83 (a)
<i>p</i> -Toluidine	5.98	-.17	2	74
<i>m</i> -Toluidine	4.73	-.07	2	81
Aniline	4.63	0.0	2	74 (a)
<i>m</i> -Anisidine	4.23	.12	2	63
<i>p</i> -Chloroaniline	4.15	.23	2	70 (a,b)
<i>m</i> -Chloroaniline	3.46	.37	2	67
Ethyl <i>p</i> -Aminobenzoate	-----	.45	4	36
δ,δ,δ -Trifluoro- <i>m</i> -toluidine	-----	.43	>4	0
<i>p</i> -Aminobenzonitrile	-----	.69	>4	0
<i>m</i> -Nitroaniline	2.466	.71	>4	0
<i>p</i> -Nitroaniline	1.00	.78	>4	0

(a) These are improved yields over those reported earlier by optimization of the procedure, R. M. Ottenbrite and P. V. Alston, *J. Org. Chem.*, 37, 3360 (1972). (b) Gschwend and Haider obtained a 47% yield with a reaction time of 3 days; H. W. Gschwend and H. Haider, *J. Org. Chem.*, 37, 59 (1972). (c) "CRC Handbook of Chemistry and Physics," 50th Ed., Chemical Rubber Co., Cleveland, Ohio, 1969, p. 115. (d) σ values from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

These dimeric compounds were characterized by nmr, mass spectrometry, and elemental analysis. The existence of the trimer was confirmed by the mass spectrum of the residue still remaining.



The limiting factor observed in these decompositions appears to be the volatility of the exocyclic diene. Since these dienes dimerize readily at the temperature required to decompose their sulfone precursor, it was necessary to collect them on the cold finger of a sublimator. If the diene, however, did not vaporize readily, considerable amounts of dimer was formed. This was observed specifically in the decomposition of 5-(carboethoxyphenyl)-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxide which gave only 18% of the exocyclic diene but 82% of the dimer.

These exocyclic dienes reacted rapidly with acrolein and maleic anhydride to give the corresponding Diels-Alder adducts VII and VIII in excellent yields:

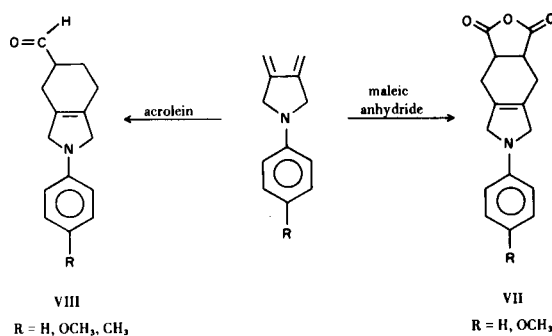
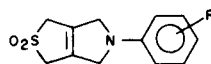


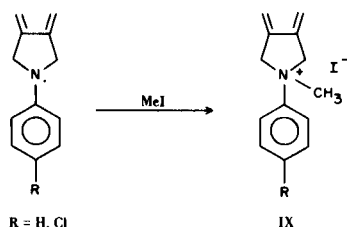
TABLE II
5-Aryl-1,3,4,6-tetrahydrothieno[3,4-c]pyrrole 2,2-Dioxides



R	Dec., °C	Molecular Formula	Elemental Analysis						NMR Spectra (a)	
			Calculated			Found			Solvent	Chem. Shift
			C	H	N	C	H	N		
<i>p</i> -(CH ₃) ₂ N	163	C ₁₄ H ₁₈ N ₂ O ₂ S	60.40	6.46	10.06	60.46	6.14	10.17	F ₃ CCOOD:	8.00 (s, 4H), 5.06 (m, 4H), 4.33 (m, 4H), 3.56 (s, 6H)
<i>p</i> -CH ₃	157	C ₁₃ H ₁₅ NO ₂ S	62.70	6.07	5.62	63.10	5.81	5.48	CDCl ₃ :	7.09 and 6.44 (AB, J = 9 Hz, 4H), 4.15 (s, 4H), 3.88 (s, 4H), 2.27 (s, 3H)
<i>m</i> -CH ₃	153	C ₁₃ H ₁₅ NO ₂ S	62.80	5.84	5.59	62.62	6.07	5.62	CDCl ₃ :	7.3-6.2 (m, 4H), 4.3-3.8 (two broad singlet, 8H), 2.3 (s, 3H)
<i>m</i> -OCH ₃	153	C ₁₃ H ₁₅ NO ₃ S	58.85	5.70	5.28	58.54	5.79	5.19	DMSO-d ₆ :	7.17-6.00 (m, 4H), 4.17-3.9 (m, 8H), 3.72 (s, 3H)
<i>m</i> -Cl	165	C ₁₂ H ₁₂ NO ₂ SCl	53.44	4.49	5.19	53.20	4.31	4.90	F ₃ CCOOD:	7.83-7.53 (m, 4H), 5.04 (m, 4H), 4.31 (m, 4H)
<i>p</i> -EtOOC	159	C ₁₅ H ₁₇ NO ₄ S	58.60	5.57	4.56	58.61	5.58	4.46	CDCl ₃	7.99 and 6.51 (AB, J = 9 Hz, 4H), 4.50-3.83 (m, 10H), 1.37 (t, J = 7 Hz, 3H)

(a) Chemical shifts (δ) are relative to TMS ($\delta = 0.0$). Signals are designated as follows: s, singlets; t, triplet; m, multiplet.

These exocyclic dienes also readily formed the corresponding 1-aryl-1-methyl-3,4-dimethylenepyrrolidinium iodides (IX) with methyl iodide:



An interesting result was obtained in the case of 1-(*p*-dimethylaminophenyl)-3,4-dimethylenepyrrolidine. This compound when reacted with methyl iodide, yielded only

a trace amount of the pyrrolidinium compound (determined by nmr) while an excellent yield (86%) of trimethyl-*p*-(3,4-dimethylenepyrrolidino)phenylammonium iodide (X) was recovered.

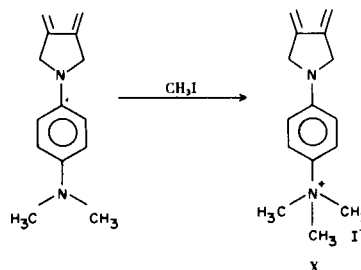
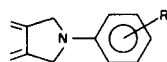


TABLE III
1-Aryl-3,4-dimethylenepyrrolidines



R	M.p. °C	% Yield	Molecular Formula	Elemental Analysis						NMR Spectra (b)
				Calculated			Found			
				C	H	N	C	H	N	
<i>p</i> -(CH ₃) ₂ N	---- (a)	45	C ₁₄ H ₁₈ N ₂	78.46	8.47	13.07	78.13	8.61	13.08	8.02 (s, 4H), 6.01 (m, 2H), 5.51 (m, 2H), 4.78 (m, 4H), 3.55 (s, 6H)
<i>p</i> -CH ₃ O	---- (a)	74	C ₁₃ H ₁₅ NO	77.61	7.52	6.95	77.86	7.77	7.02	6.90 and 6.56 (AB, J = 9 Hz, 4H), 5.53 (m, 2H), 5.07 (m, 2H), 4.03 (m, 4H), 3.77 (s, 3H)
<i>p</i> -EtOOC	---- (a)	18	C ₁₅ H ₁₇ NO ₂	74.05	7.04	5.76	73.90	7.03	5.53	7.97-6.52 (AB, J = 9 Hz, 4H), 5.58 (m, 2H), 5.09 (m, 2H), 4.34 (q, J = 7 Hz, 2H), 4.16 (m, 4H), 1.37 (t, J = 7 Hz, 3H)
<i>p</i> -CH ₃	---- (a)	71	C ₁₃ H ₁₅ N	84.28	8.16	7.56	84.05	8.39	7.42	7.10 and 6.54 (AB, J = 9 Hz, 4H), 5.55 (m, 2H), 5.07 (m, 2H), 4.06 (m, 4H), 2.27 (s, 3H)
<i>m</i> -CH ₃	62-64	82	C ₁₃ H ₁₅ N	84.28	8.16	7.56	83.94	8.35	7.44	7.33-6.29 (m, 4H), 5.55 (m, 2H), 5.07 (m, 2H), 4.10 (m, 4H), 2.34 (s, 3H)
<i>m</i> -CH ₃ O	75-76	60	C ₁₃ H ₁₅ NO	77.61	7.52	6.95	77.96	7.64	6.96	7.38-7.04 and 6.58-6.09 (m, 4H), 5.57 (m, 2H), 5.08 (m, 2H), 4.10 (m, 4H), 3.82 (s, 3H)
<i>m</i> -Cl	42-45	61	C ₁₂ H ₁₂ NCl	70.08	5.88	6.81	70.17	6.03	6.63	7.33-6.30 (m, 4H), 5.55 (m, 2H), 5.07 (m, 2H), 4.07 (m, 4H)
H	---- (a)	74	C ₁₂ H ₁₃ N	84.16	7.64	8.17	83.92	7.83	8.13	7.45-6.48 (m, 5H), 5.55 (m, 2H), 5.07 (m, 2H), 4.09 (m, 4H)

(a) Melting point not detectable due to dimerization and polymerization. (b) Determined with deuteriochloroform solution except 1-(*p*-dimethylaminophenyl)-3,4-dimethylenepyrrolidine for which deuteriotrifluoroacetic acid was used. Chemical shifts (δ) are relative to TMS ($\delta = 0.0$). Signals are designated as follows: s, singlet; t, triplet; q, quartet; m, multiplet.

EXPERIMENTAL

Melting points were obtained in a Thomas-Hoover melting point apparatus and are uncorrected. Nmr spectra were recorded on a Varian A-60 and a Perkin-Elmer R-24 with TMS as internal reference. It spectra (potassium bromide pellets) were recorded on Perkin-Elmer 337 and elemental analysis were carried out on a Perkin-Elmer 240. Uv spectra were recorded on a Beckman DK-2. All the compounds in Table II were prepared by essentially the same procedure as that given below for 5-(*p*-methylphenyl)-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxide. The compounds in Table III were prepared by the same procedure as that given below for 1-phenyl-3,4-dimethylenepyrrolidine.

5-(*p*-Methylphenyl)-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-Dioxide (II).

The dibromosulfone (I) (6.08 g., 20 mmoles) was dissolved in 250 ml. of boiling methanol. Sodium carbonate (2.21 g., 20 mmoles) and *p*-toluidine (2.14 g., 20 mmoles) were added to hot methanol solution. The solution was refluxed for one hour and then allowed to cool to room temperature. During this time all the sodium carbonate was consumed and most of the bicyclic product (II) precipitated out of solution (3.6 g. recovered by filtration). The reaction solution was now allowed to stand in a freezer overnight and another 0.1 g. of bicyclic product was

recovered. Total yield was 74%; dec. 157°; ν max 1619, 1515, 1364, 1292, 1180, 1105, 1096, 790 cm^{-1} .

5-(*p*-Methylphenyl)-1,3-dihydrothieno[3,4-*c*]pyrrole 2,2-Dioxide (III).

The reaction solution (from the above procedure) was evaporated to a volume of 30 ml. and was again allowed to stand in a freezer overnight. The oxidized product, 0.5 g. (10% yield) was recovered by filtration, m.p. 202-204°; ν max 1515, 1350, 1303, 1195, 1120, 1091, 1030, 805, 774 cm^{-1} ; nmr (deuteriochloroform): δ 7.26 (s, 4H), 6.96 (s, 2H), 4.23 (s, 4H), 2.40 (s, 3H).

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$: C, 63.13; H, 5.29; N, 5.66. Found: C, 63.08; H, 5.39; N, 5.60.

5-Phenyl-1,3-dihydrothieno[3,4-*c*]pyrrole 2,2-Dioxide (III).

This compound was similarly isolated as a minor product from the reaction of aniline with I. Yield was 9%, m.p. 210-211°; ν max 1595, 1495, 1300, 1200, 1120, 760 cm^{-1} ; nmr (deuteriochloroform): δ 7.42 (s, 5H), 7.01 (s, 2H), 4.25 (s, 4H).

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{S}$: C, 61.8; H, 4.75; N, 6.01. Found: C, 62.17; H, 4.54; N, 5.94.

1-Phenyl-3,4-dimethylenepyrrolidene (IV).

5-Phenyl-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-dioxide (2.0 g.) was placed in a sublimator and heated to 145° under reduced pressure (0.1 mm) for six hours. A mixture of the exocyclic diene and rearranged product was recovered from the cooled finger of the sublimator. Pure diene was obtained by recrystallization from ether-petroleum ether. Yield was 1.0 g. (74%); ν max 246, 299 μ (ϵ 26660, 4450).

1-Phenyl-3,4-dimethylpyrrole (V).

The ether-petroleum ether solution (from the above procedure) which was enriched with the rearranged product was extracted with 50 ml. of 3*N* aqueous hydrochloric acid. After drying with magnesium sulfate, the solution was evaporated to dryness yielding only the rearranged product. Yield was 0.04 g. (3%), m.p. 63-65°, lit. (5) 71-72°; nmr and ir spectra agree with those of Jones *et al.* (6,7).

Dimer (VI) of 1-(*p*-Methoxyphenyl)-3,4-dimethylenepyrrolidine.

The dimer was obtained by sublimation of the residue left after decomposition of the bicyclic compound. The residue was sublimed at 200° for 12 hours. Yield was 13%, dec. 193°; ν max 1511, 1368, 1232, 1036, 815 cm^{-1} ; nmr (deuteriotrifluoroacetic acid): δ 7.7-7.0 (m, 8H), 5.7-5.3 (m, 2H), 5.1-3.8 (m, 14H), 2.8-2.1 (m, 6H).

Anal. Calcd. for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_2$: C, 77.6; H, 7.52; N, 6.95. Found: C, 77.5; H, 7.56; N, 6.95.

Dimer (VI) of 1-(*p*-Methylphenyl)-3,4-dimethylenepyrrolidine.

This dimer was obtained by the same procedure as above. Yield was 8%, dec. 199°; ν max 1618, 1516, 1466, 1362, 795 cm^{-1} ; nmr (deuteriotrifluoroacetic acid): δ 7.62 (m, 8H), 5.90-3.80 (m, 10H), 3.4-1.7 (m, 12H).

Anal. Calcd. for $\text{C}_{26}\text{H}_{30}\text{N}_2$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.77; H, 8.17; N, 7.67.

Diels-Alder Adduct (VII) of 1-Phenyl-3,4-dimethylenepyrrolidine with Maleic Anhydride.

The diene (0.4 g., 2.34 mmoles) and maleic anhydride (0.23 g., 2.34 mmoles) were dissolved in 50 ml. of anhydrous ether. The solution was stirred for 24 hours at room temperature during which time the adduct precipitated from solution. Yield was

0.63 g. (62%), dec. 229-230°; ν max 1855, 1775, 1595, 1370, 1219, 958, 905, 754, 692 cm^{-1} ; nmr (deuteriotrifluoroacetic acid): δ 7.64 (m, 5H), 5.0-4.6 (m, 4H), 4.0-3.75 (m, 2H), 3.0-2.6 (m, 4H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 71.45; H, 5.62; N, 5.20. Found: C, 71.32; H, 5.56; N, 5.32.

Diels-Alder Adduct (VII) of 1-(*p*-Methoxyphenyl)-3,4-dimethylenepyrrolidine with Maleic Anhydride.

The adduct was prepared by the same procedure as the previous one. Yield was 50%, m.p. 157-159°; ν max 1850, 1768, 1510, 1373, 1235, 1220, 940, 890, 804 cm^{-1} ; nmr (deuteriotrifluoroacetic acid): δ 7.53 and 7.18 (AB, $J = 9$ Hz, 4H), 5.0-4.6 (m, 4H), 4.15-3.7 (m, 2H; s, 3.98, 3H), 3.0-2.65 (m, 4H).

Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_4$: C, 68.25; H, 5.72; N, 4.68. Found: C, 68.27; H, 5.73; N, 4.50.

Diels-Alder Adduct (VIII) of 1-Phenyl-3,4-dimethylenepyrrolidine with Acrolein.

The diene (0.5 g.) was dissolved into a 6 ml. solution of 50% methylene chloride and 50% acrolein. The reaction mixture was allowed to stand at room temperature for 3 hours after which time it was evaporated to dryness. The residue was recrystallized in petroleum ether to yield the adduct (0.6 g., 90%), m.p. 113-114°; ν max 1715, 1595, 1500, 1450, 1370, 724, 692 cm^{-1} ; nmr (deuteriochloroform): δ 9.72 (s, 1H), 7.50-6.30 (m, 5H), 3.98 (s, 4H), 2.8-1.7 (m, 7H).

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}$: C, 79.3; H, 7.54; N, 6.16. Found: C, 79.48; H, 7.66; N, 5.98.

Diels-Alder Adduct (VIII) of 1-(*p*-Methoxyphenyl)-3,4-dimethylenepyrrolidine with Acrolein.

This adduct was prepared by the same procedure as above. Yield was 90%, m.p. 129-130°; ν max 1717, 1509, 1371, 1220, 1030, 802 cm^{-1} ; nmr (deuteriochloroform): δ 9.72 (s, 1H), 6.0 and 6.55 (AB, $J = 9$ Hz, 4H), 4.01 (m, 4H), 3.77 (s, 3H), 2.4-1.8 (m, 7H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}_2$: C, 74.7; H, 7.44; N, 5.41. Found: C, 75.03; H, 7.41; N, 5.40.

Diels-Alder Adduct (VIII) of 1-(*p*-Methylphenyl)-3,4-dimethylenepyrrolidine with Acrolein.

This adduct was prepared by the same procedure previously described. Yield was 95%, m.p. 109-110°; ν max 1725, 1621, 1518, 1370, 799 cm^{-1} ; nmr (deuteriochloroform): δ 9.72 (s, 1H), 7.17 and 6.57 (AB, $J = 9$ Hz, 4H), 4.0 (s, 4H), 2.8-1.7 (m, 10H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}$: C, 79.60; H, 7.92; N, 5.8. Found: C, 79.20; H, 7.94; N, 5.58.

1-Phenyl-1-methyl-3,4-dimethylenepyrrolidinium Iodide (IV).

The diene (0.4 g.) was dissolved in 3 ml. of methyl iodide. This solution was allowed to stand for 24 hours during which time a precipitate formed. The reaction mixture was diluted with ether and the product was collected by filtration. Upon recrystallization in methanol-ether, 0.6 g. (82%) of the salt was obtained, softens at 187-189° and melts into a viscous liquid 210-215°; ν max 1588, 1490, 1452, 1440, 1427, 914, 759, 692 cm^{-1} ; nmr (DMSO- d_6): δ 7.75 (m, 5H), 5.98 (m, 2H), 5.55 (m, 2H), 4.98 (m, 4H), 4.65 (s, 3H).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{IN}$: C, 49.85; H, 5.15; N, 4.47. Found: C, 50.00; H, 4.80; N, 4.30.

1-(*p*-Chlorophenyl)-1-methyl-3,4-dimethylenepyrrolidinium Iodide (IX).

The procedure was the same as above except the reaction time was 36 hours and 50% of the diene was unreactive. Yield was 60% (based on reacted diene), dec. 212-214°; ir ν max 1491, 1431, 1411, 1119, 1088, 1007, 908, 833 cm^{-1} ; nmr (DMSO- d_6): δ 7.99 and 7.73 (AB, $J = 9$ Hz, 4H), 5.95 (m, 2H), 5.45 (m, 2H), 5.5-4.8 (broad AB, 4H), 3.99 (s, 3H).

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{ClIN}$: C, 44.91; H, 4.35; N, 4.03. Found: C, 44.99; H, 4.44; N, 3.99.

Trimethyl-*p*-(3,4-dimethylenepyrrolidino)phenylammonium Iodide (X).

The diene (0.35 g.) was dissolved into 4 ml. of methyl iodide. This solution was allowed to stand for 15 hours during which time a precipitate formed. The reaction mixture was diluted with ether and the precipitate was collected by filtration. The precipitate was washed with 8 ml. of methanol and the remaining residue was recrystallized in methanol-ether to yield 0.5 g. (86%) of the product, dec. 206-207°; ir ν max 1611, 1516, 1470, 1375, 1202, 912, 810 cm^{-1} ; nmr (DMSO- d_6): δ 7.79 and 6.70 (AB, $J = 9$ Hz, 4H), 5.64 (m, 2H), 5.14 (m, 2H), 4.14 (m, 4H), 3.55 (s, 9H).

Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{IN}_2$: C, 50.57; H, 5.94; N, 7.87. Found: C, 50.5; H, 5.96; N, 7.80.

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