1-(*p*-Chlorophenyl)-3,4-dimethylenepyrrolidine, a New Pyrrole Isomer

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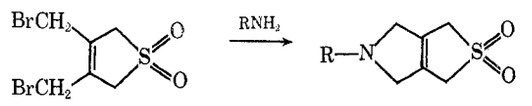
1-(*p*-Chlorophenyl)-3,4-dimethylenepyrrolidine, isomeric with the corresponding pyrrole, was prepared. The key step involves the SO_2 extrusion of a bicyclic sulfolene under reduced pressure. The structure of the diene was confirmed by its spectral data as well as by conversion to a dimer and two Diels–Alder adducts.

The synthesis and characteristics of the reactive double bond isomer of *o*-xylene, 4,5-dimethylenecyclohexene, have been reported.[1] Among the corresponding isomers of the five-membered oxygen, sulfur, and nitrogen heterocycles, only 3,4-dimethylenetetrahydrofuran has been accessible to date.[2] The present article describes the preparation and characteristics of 1-(*p*-chlorophenyl)-3,4-dimethylenepyrrolidine, a new double bond isomer of 3,4-dimethylpyrrole.

A rather effective way of masking a diene is its cycloaddition to sulfur dioxide. This cheletropic,[3] reversible reaction has found great synthetic utility not only for the preparation of sulfones[4] but in particular for stereospecific syntheses and protection of dienes and polyenes.[5–8]

3,4-Bis(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide (**1**), which is easily obtained by brominating the cycloaddition product of 2,3-dimethyl-1,3-butadiene and sulfur dioxide,[9] seemed to be an attractive precursor for a masked 3,4-dimethylenepyrrolidine (**2**).



1 **2**

However, reaction of the dibromide **1** with various primary amines under very mild conditions in either protic or nonprotic solvents produced only intractable mixtures. A possible explanation for these results would be that the strongly acidic character of the sulfolene protons toward the amines strongly favors proton abstraction and thus virtually suppresses the nucleophilicity of the amines.

A 1,4-HBr elimination from **1** would then yield rather reactive dienes, prone to undergo secondary reactions. By reacting **1** with a weakly basic amine, such as *p*-chloroaniline (pK_a 3.97), in either a protic or a nonprotic solvent, the bicyclic sulfolene **2a** (R = *p*-Cl-C_6H_4) was obtained in moderate yield. Its nmr spectrum with singlets at δ 4.03 and 4.16 ppm, respectively, each accounting for 4 protons, leaves no doubt about the symmetry of the structure. In trifluoroacetic acid, the signals of the hydrogens adjacent to the now-protonated N shift to lower field (4.97 ppm). A low-temperature mass spectrum (100°) exhibits the molecular ion at 269 as well as *m/e* 205, the reaction product of the sulfur dioxide extrusion. Catalytic reduction of **2a** produces a nicely crystalline dihydro derivative **3**. **2a** is stable in its crystalline state at room temperature over extended periods of time. In solution, however, it is slowly oxidized to the pyrrole **4**, a reaction which preparatively and reproducibly can be achieved (60%) by stirring a solution of **2a** in CH_2Cl_2 with an excess of an ethanolic solution of $(NH_4)_2Ce(NO_3)_6$ for a short period of time. The assignment of the pyrrole structure **4** as opposed to the possible alternative (thiophene 1,1-dioxide) is corroborated as follows. (a) The uv [λ_{max} 263 mμ (ϵ 20,400)] and ir spectra[10] are compatible with 1-*p*-chlorophenyl pyrrole. (b) The pyrrole protons in the nmr shift from δ 6.95 ($CDCl_3$) to 11.4 ppm (2 H) in CF_3COOH, whereas the sulfolene hydrogens remain virtually in the same area (4.20 and 4.42 ppm, respectively). (c) The properties of **4** would not be compatible with the reported[11,12] instability of thiophene 1,1-dioxides.

Thermolysis of **2a** leads to rapid and clean SO_2 extrusion. Upon heating **2a** beyond its decomposition point (148–155°), the material resolidifies. An nmr spectrum of this crude and rather insoluble material (CF_3COOD) agrees quite well with the Diels–Alder adduct **6** of the initially formed diene **5**. At δ 2.1–2.8 there are the signals (broad) for two allylic CH_2 groups: at 4.1 the peak of the nonallylic CH_2 adjacent to the N, at 4.6–4.9 the absorption for 3 allylic CH_2's adjacent to N, at 5.5 the geminal vinyl protons, and finally at 7.6 ppm the 8 aromatic hydrogens. A mass spectrum of this material at 205° clearly reveals it to be a dimer (M^+ 410). The next major fragment is *m/e* 204, *i.e.*, one mass unit short of the monomer **5** and thus probably not a molecular ion. Further confirmation of structure **6** is obtained by observing a spectrum at 300°; it still reveals M^+ 410 (dimer **6**) as well as some trimeric material (M^+ 615) and now a relatively strong M^+ at 205, attributable to the thermal retro-Diels–Alder reaction.[13]

Practical preparation of the diene **5** is brought about simply by subliming the bicyclic sulfolene **2** at 135–138° (0.1 mm); the crystalline diene can be collected in 79% yield. The residue again is dimeric and trimeric material. **5** is a relatively stable compound and

(1) W. J. Bailey and J. Rosenberg, *J. Amer. Chem. Soc.*, **77**, 73 (1955).

(2) (a) W. J. Bailey and S. S. Miller, *J. Org. Chem.*, **28**, 802 (1963); (b) E. J. Fetter, *Diss. Abstr.*, **22**, 2985 (1962) [*Chem. Abstr.*, **57**, 758e (1963)]; only indirect evidence is presented for the formation (3–5%) of 3,4-dimethylenethiophane by pyrolysis of 3,4-bis(acetoxymethyl)thiophane.

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(4) (a) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York and London, 1967, pp 13–45; (b) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967); (c) O. Grummit and A. L. Endrey, *ibid.*, **82**, 3614 (1960).

(5) (a) W. L. Mock, *ibid.*, **88**, 2857 (1966); (b) *ibid.*, **91**, 5682 (1969); (c) *ibid.*, **92**, 3807 (1970); (d) *ibid.*, **92**, 6918 (1970).

(6) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(7) E. J. Corey, N. H. Anderson, R. M. Carlson, E. Vedejs, J. Paust, I. Vlattas, and R. E. K. Winter, *ibid.*, **90**, 3245 (1968).

(8) P. Dowd, *ibid.*, **92**, 1066 (1970).

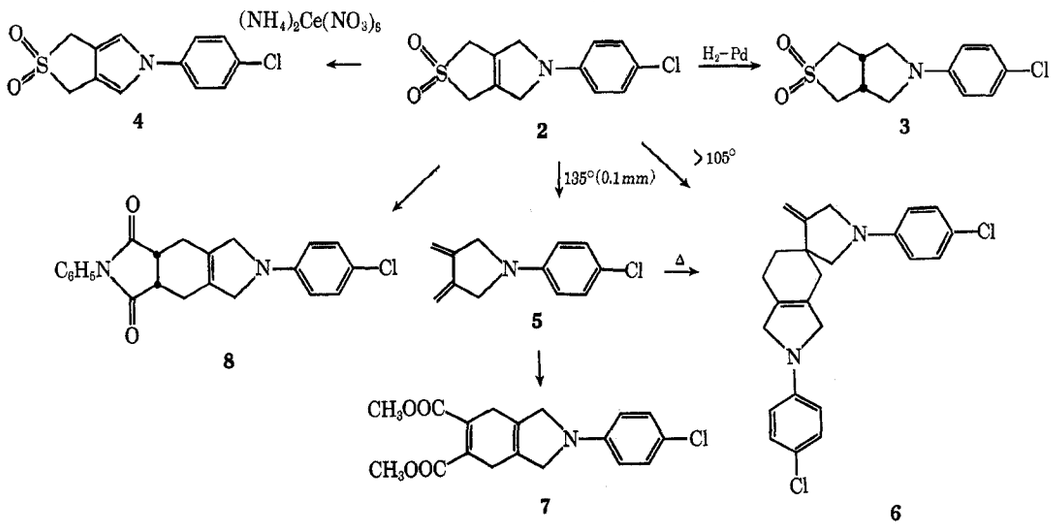
(9) G. B. Butler and R. M. Ottenbrite, *Tetrahedron Lett.*, 4873 (1967).

(10) (a) Ir of 1-(*p*-chlorophenyl)-3,4-dimethylpyrrole [R. A. Jones, *Aust. J. Chem.*, **19**, 289 (1966)]; (b) uv of 1-phenylpyrrole [253 mμ (log ϵ 4.3)] [J. Davoll, *J. Chem. Soc.*, 3802 (1953)].

(11) (a) W. L. Mock, *J. Amer. Chem. Soc.*, **92**, 7610 (1970); (b) L. A. Carpino, L. V. McAdams, R. H. Rynbrandt, and J. W. Spiewak, *ibid.*, **93**, 476 (1971).

(12) (a) W. J. Bailey and E. W. Cummins; *ibid.*, **76**, 1932 (1954); (b) J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **72**, 314 (1953).

(13) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).



can be stored in its crystalline state. By warming a solution of the diene, polymeric material is formed quite readily. The most evident proof for structure **5** is obtained by its nmr spectrum. The methylene hydrogens adjacent to the N appear as an apparent triplet at 4.05 ppm with an allylic coupling of $J \cong 2$ Hz. Each pair of equivalent vinyl protons exhibits a triplet (J = 2 Hz) at 5.05 (exo proton) and at 5.52 ppm (J = 2 Hz) (endo proton). Finally, the aromatic hydrogens show the expected AB system, centered at δ 6.5 and 7.55 ppm, respectively (J = 9 Hz). The spectrum of **5** is thus in good agreement with the one reported for tetrahydro-3,4-dimethylenefuran.[2]

The isomerization of the diene **5** into the aromatic pyrrole has not been observed, either thermally (only oligomeric products formed) or by acid catalysis. The stability of **5** toward acids is demonstrated by observing its nmr spectrum in CF_3COOD: except for a downfield shift of the aliphatic and vinyl protons, the very characteristic pattern remains unchanged. The ir spectrum of the diene **5** has a strong band at 890 cm^{-1} (out of plane deformation frequency) and at 810 cm^{-1}. The ultraviolet spectrum of **5** reflects the superimposed absorptions of the diene and *p*-chloroaniline chromophores with a λ_{max} at 253 mμ (ϵ 25,800) and 306 (4400). By subtracting the spectrum of *p*-chloro-*N*,*N*-dimethylaniline[14] one obtains a λ_{max} in the area of 240–260 mμ with an extinction coefficient of 9000, a result which is compatible with the λ_{max} 244 mμ (ϵ 9820) reported[2] for tetrahydro-3,4-dimethylenefuran. The mass spectrum of the diene once again reveals its thermal reactions: at 265° the most intense molecular ion is at 410 (dimer), whereas M^+ 205 is only a minor peak. Again, *m/e* 204 is attributed to a fragmentation of the dimer, rather than to a M − 1 loss of the monomeric diene **5**. At 50° the spectrum shows no dimer and the "normal" fragmentation pattern of **5** can be observed with peaks at M^+ 205 and *m/e* 190, 154, 138, 111.

Some chemical evidence was gained by forming the Diels–Alder adduct **7** of the diene with dimethyl acetylenedicarboxylate. The Diels–Alder reaction can be carried out directly on the masked diene **2** as has been shown by heating equimolar amounts of **2** and *N*-phenylmaleimide in refluxing xylene. The adduct **8** was obtained in a considerably higher yield than by the stepwise procedure **2a** → **5** → **7**. This is an appealing preparative aspect in the reaction of dienophiles with rather unstable 1,3-dienes, as had been demonstrated by other investigators.[15,16]

(14) *p*-Chloro-*N*,*N*-dimethylaniline, λ_{max} 260 mμ (ϵ 15,900): P.r Gammaticakis, *Bull. Soc. Chim. Fr.*, 534 (1951).

Experimental Section[17]

5-(*p*-Chlorophenyl)-1,3,4,6-tetrahydrothieno[3,4-*c*]pyrrole 2,2-Dioxide (2a).—The dibromo sulfone **1** (12 g, 40 mmol) and 5.1 g (40 mmol) of *p*-chloroaniline were stirred in 250 ml of CH_2Cl_2 with 8.45 g of anhydrous Na_2CO_3 for 3 days at room temperature. After filtration from the inorganic solid, the solvent was removed *in vacuo*. The crude residue (15.45 g) was boiled in ethanol, and after cooling two crops of the bicyclic product **2a** (4.2 and 0.9 g, dec pt 147–149°) were obtained (47%). From the mother liquors 1.85 g of the unreacted dibromo sulfone **1** (12%) could be recovered. An analytical sample was obtained by washing the bicyclic sulfone with hot ethanol or by recrystallizing it from CH_2Cl_2: both operations raised the decomposition point to 153°; ν_{max}^{Nujol} 1600, 1500, 1370, 1290, 1187, 1110, 1085, 770 cm^{-1}; nmr (CF_3COOD) δ 4.22 (s, 4 H), 4.97 (s, 4 H), 7.62 ppm (s, 4 H); nmr (DMFA-d_6) 4.03 (s, 4 H), 4.16 (s, 4 H), 6.55 and 7.22 ppm (AB, J = 9 Hz, 4 H); mass spectrum (100°) M^+ 269, *m/e* 205, 138, 111.

Anal. Calcd for $C_{12}H_{12}ClNO_2S$: C, 53.44; H, 4.49; N, 5.19. Found: C, 53.13; H, 4.59; N, 4.91.

5-(*p*-Chlorophenyl)-1,3,3a,4,6,6a-hexahydrothieno[3,4-*c*]-pyrrole 2,2-Dioxide (3).—A solution of 4 g (16 mmol) of bicyclic sulfone in 200 ml of ethanol was hydrogenated over 800 mg of 10% Pd/C at 30 lb of hydrogen pressure for 2 hr. After filtration and removal of some ethanol, the product crystallized: 2.6 g (65%); mp 174–175°; ν_{max}^{Nujol} 1600, 1500, 1375, 1310, 1305, 1130, 1110, 800 cm^{-1}; nmr ($CDCl_3$) δ 2.9–3.7 (m, 10 H), 6.53 and 7.2 ppm (AB, J = 9 Hz, 4 H).

Anal. Calcd for $C_{12}H_{14}ClNO_2S$: C, 53.08; H, 5.20; N, 5.16. Found: C, 52.80; H, 5.24; N, 5.05.

5-(*p*-Chlorophenyl)-1,3-dihydrothieno[3,4-*c*]pyrrole 2,2-Dioxide (4).—To a solution of 600 mg (2.23 mmol) of bicyclic sulfone **2a** in 30 ml of CH_2Cl_2 was added a freshly prepared solution of 2.5 g of $(NH_4)_2Ce(NO_3)_6$ in 60 ml of ethanol. After the mixture was stirred for 30 min at room temperature the solvent was removed, and the residue was taken up in CH_2Cl_2 and washed with water. After drying over Na_2SO_4 and removal of the solvent, the residue was filtered through a column of 24 g of silica gel, using $CHCl_3$. The first fraction of 150 ml was evaporated and its residue (400 mg) crystallized from CH_2Cl_2–ether to yield 360 mg of product (60%), mp 176–177°, as white crystals: ν_{max}^{Nujol} 1520, 1500, 1310, 1200, 1130, 825, 790 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 263 mμ (ϵ 20,400); nmr ($CDCl_3$) δ 4.20 (s, 4 H), 6.95 (s, 2 H), 7.35 ppm (AB, J = 9 Hz,

(15) I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).

(16) L. F. Hatch and D. Peter, *Chem. Commun.*, 1499 (1968).

(17) Melting points were obtained in a Thomas-Hoover melting point apparatus and are uncorrected. Nmr spectra were recorded on a Varian A-60 instrument, ir spectra on a Perkin-Elmer 521, and uv curves on a Cary Model 14. The mass spectra were recorded on an AEI MS 902 by direct insertion.

4 H); nmr (CF_3COOD) 4.42 (s, 4 H), 7.35 (AB, J = 9 Hz, 4 H), 11.4 ppm (s, 2 H).

Anal. Calcd for $C_{12}H_{10}ClNO_2S$: C, 53.84; H, 3.76; N, 5.23. Found: C, 53.52; H, 3.97; N, 5.25.

1-(*p*-Chlorophenyl)-3,4-dimethylenepyrrolidine (5).—The sulfone **2a** (500 mg) was left under vacuum (0.1 mm) and 135–138° overnight. The diene sublimed and was collected (300 mg, 79%). The crystalline residue (dimer) amounted to 80 mg (21%). The sublimed diene was virtually pure, the only impurities being traces of dimeric and polymeric material. The 300 mg were recrystallized from ether–hexane (without excessive heating) to give a first crop of 110 mg (melting point not detectable due to dimerization upon heating): ν_{max}^{Nujol} 1600, 1500, 1100, 900, 890, 810 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 253 mμ (ε 25,780), 306 (4420); nmr ($CDCl_3$) δ 4.05 (~t, J = 2 Hz, 4 H), 5.05 (~t, J = 2 Hz, 2 H), 5.52 (t, J = 2 Hz, 2 H), 6.5 and 7.18 (AB, J = 9 Hz, 4 H); nmr (CF_3COOD) 4.7 (m, broad, 4 H), 5.43 (m, broad, 2 H), 5.93 (m, broad, 2 H), 7.55 ppm (s, 4 H); mass spectrum (50°) M^+ 205, *m/e* 190, 168, 154, 138, 111.

Anal. Calcd for $C_{12}H_{12}ClN$: C, 70.08; H, 5.88; N, 6.81. Found: C, 70.18; H, 5.94; N, 6.57.

Dimer of 1-(*p*-Chlorophenyl)-3,4-dimethylenepyrrolidine 6.—The dimer of **5** was obtained as a side product in the preparation of **5** (see above). By heating the sulfolene **2a** for 5 min in an oil bath of 170°, a complete conversion into crude **6** is observed (dec 220°). Owing to very poor solubility, purification of the dimer **6** was not feasible: nmr (CF_3COOD) δ 2–2.8 (m, 6 H), 4.1 (m, 2 H), 4.6–4.9 (m, 6 H), 5.5 (m, 2 H), 7.6 (m, 8 H); mass spectrum (205°) M^+ 410, *m/e* 204, 140, 138, 111; mass spectrum (300°) M^+ 613, 410, 205, *m/e* 270, 242, 218, 204, 190, 140, 138, 125, 111.

Diels–Alder Adduct with Dimethyl Acetylenedicarboxylate (7).—A solution of 860 mg (4.2 mmol) sublimed diene **5** and 1.5 ml (12 mmol) of dimethyl acetylenedicarboxylate in 10 ml of dry toluene was refluxed for 20 hr. After evaporation of the solvent the residue is crystallized from ether to give 720 mg of diester (mp 189–191°) (50%). Recrystallization of 500 mg thereof from CH_2Cl_2–ether gave 350 mg (mp 189–191°): ν_{max}^{Nujol} 1740, 1720, 1705, 1650, 1500, 1280, 1060, 810 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 260 mμ (ε 24,890), 315 (2490); nmr ($CDCl_3$) δ 3.05 (s, 4 H), 3.76 (s, 6 H), 3.94 (s, 4 H), 6.35 and 7.13 (AB, J = 9 Hz, 4 H).

Anal. Calcd for $C_{18}H_{18}ClNO_4$: C, 62.21; H, 5.22; N, 4.04. Found: C, 62.54; H, 5.35; N, 4.08.

Diels–Alder Adduct with *N*-Phenylmaleimide (8).—A solution of 269 mg (1 mmol) of sulfone **2a** and 173 mg (1 mmol) of *N*-phenylmaleimide in 2.5 ml of xylene was refluxed under nitrogen for 3 hr. The mixture was then cooled and diluted with some benzene, and the product crystallized out: 250 mg; mp 204–206° (66%); ν_{max}^{Nujol} 1708, 1390, 795 cm^{-1}; nmr ($CDCl_3$) δ 2.7 (broad s, 4 H), 3.4 (m, 2 H), 4.04 (s, 4 H), 6.4 and 7.2 (AB, J = 9 Hz, 4 H), 7.4 (m, 5 H); mass spectrum 378 (M^+), 230, 204, 190, 138, 111.

Anal. Calcd for $C_{22}H_{19}ClN_2O_2$: C, 69.76; H, 5.05; N, 7.34. Found: C, 70.10; H, 5.13; N, 7.29.

Registry No.—**2a**, 32515-66-5; **3**, 32515-67-6; **4**, 32515-68-7; **5**, 32515-69-8; **6**, 32515-70-1; **7**, 32515-71-2; **8**, 32515-72-3.

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Allenes from Fragmentation of Tosylhydrazones

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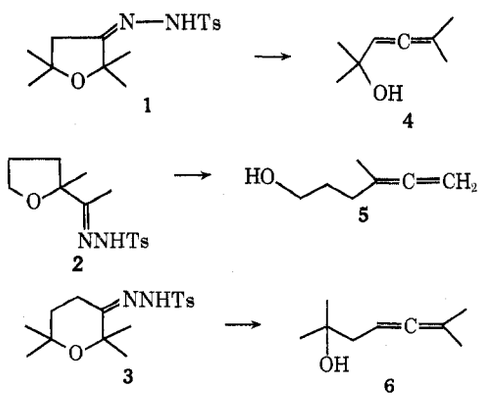
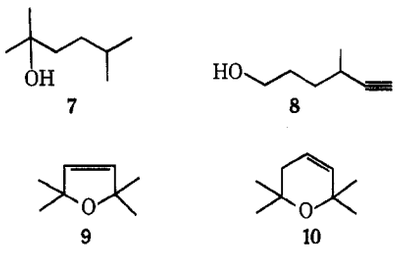
Tosylhydrazones **1**, **2**, and **3** undergo fragmentation on treatment with 2 equiv of butyllithium to form allenic alcohols **4**, **5**, and **6**. Mechanistic pathways and structural restrictions on the reaction are discussed.

We describe here the fragmentation of three α-alkoxytosylhydrazones to form the related allenes. In each case the tosylhydrazone reacted with 2 equiv of butyllithium in ether–hexane to give an allenic alcohol in 48–58% yield, **1**, **2**, and **3** leading to **4**, **5**, and **6** as indicated. These products were characterized by ir



and nmr spectroscopy; in addition, **4** was reduced over platinum to the saturated alcohol **7**, which was identical with an authentic sample.[2] Excess base favored partial isomerization of **5** to the terminal acetylene **8**, and both **1** and **3** yielded a small amount of olefinic ether (**9** and **10**, respectively) in addition to allenes.



Closely related transformations suggest two possible pathways for these fragmentations. A mechanism considered[3] for the base-catalyzed decomposition of α,β-epoxytosylhydrazones is reproduced in eq 1 and involves carbon–oxygen bond cleavage in the first step. The reaction of simple tosylhydrazones with butyl-

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(2) Authentic **7** was prepared by reaction of isopentylmagnesium bromide with acetone: L. R. C. Barclay and J. W. Hilchie, *J. Org. Chem.*, **22**, 633 (1957).

(3) A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, **50**, 708 (1967); M. Tanabe, D. F. Crowe, R. L. Dehn, and G. Detre, *Tetrahedron Lett.*, 3739 (1967).