Ring-opening reactions of pyrrolidinylcyclopropenyl cations in alkaline aqueous solution

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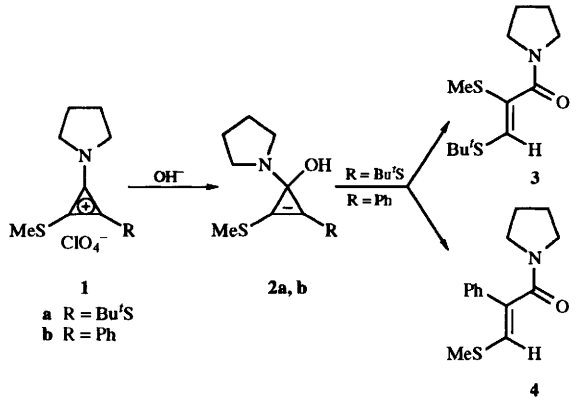
COMMUNICATION

Pyrrolidinylcyclopropenyl cations 1a,b in alkaline solution at room temperature are converted efficiently into (*Z*)- and (*E*)-α,β-unsaturated amides 3 and 4, respectively, with more electron-donating alkylsulfanyl groups at the β-position.

Recently we have reported the synthesis of 1-*tert*-butylsulfanyl-2-methylsulfanyl-3-pyrrolidinylcyclopropenylium perchlorate **1a** and 1-methylsulfanyl-2-phenyl-3-pyrrolidinylcyclopropenylium perchlorate **1b** from 2,3-bis(*tert*-butylsulfanyl)cyclopropenethione.[1] Trisubstituted pyrrolidinylcyclopropenyl cations such as **1a,b** are of interest because they may provide useful information about the addition reactions of pyrrolidinylcyclopropenyl cations with nucleophiles and any resultant ring-opening. The reaction of **1a,b** with hydroxide as a nucleophile has received little attention to date[2] and we can now report that the nucleophilic addition of hydroxide to **1a,b** occurs preferentially at the position attached to the pyrrolidinyl group to form the adducts **2a,b**. The consequent ring-opening of **2a,b**, gives the (*Z*)- and (*E*)-α,β-unsaturated amides **3** and **4**, respectively, the stereochemistry of the products being dependent on the nature of the substituents to give the more electron-donating alkylsulfanyl group at the β-position, as shown in Scheme 1.



1
a R = Bu'S
b R = Ph

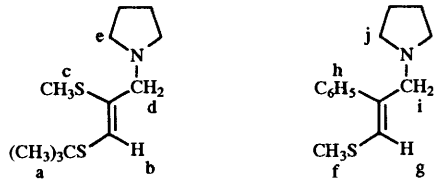
2a, b

3

4

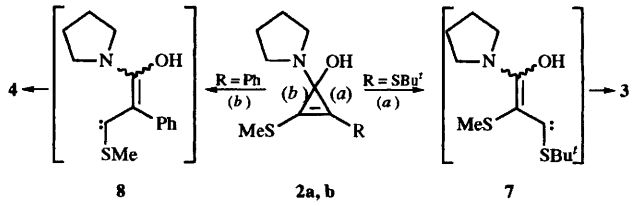
Scheme 1

A mixture of **1a** or **1b** and aqueous NaOH was stirred at room temperature for 1 h, after which chromatography on silica gel with ethyl acetate as eluent gave the ring-opened compounds **3** and **4** in 85 and 82% yields, respectively. The IR spectra of **3** and **4** showed a signal due to the C=O stretching of the amide group at 1622 and 1621 cm^{-1}, respectively. Furthermore, the ^{13}C and ^{1}H NMR spectra of **3** and **4** showed a signal for the carbonyl carbon at δ_C 165.51 and 168.26 ppm and due to the olefinic proton at δ_H 6.82 and 6.85 ppm, respectively. The stereochemistry of the double bond was determined by measuring the NOESY spectra of **5** and **6**, which were derived from **3** and **4**, respectively, by reaction with lithium aluminium hydride in dry diethyl ether. In the NOESY spectrum of **5**, cross peaks were observed between H_c (δ_H 2.36) and H_a (δ_H 1.39), H_d (δ_H 3.27) and H_e (δ_H 2.51) respectively, but not between H_c and H_b (δ_H 6.37) and H_d and H_a. This result indicates that the methylsulfanyl group is situated close to the pyrrolidinyl and methylene groups and that the methylsulfanyl and *tert*-butylsulfanyl groups are mutually *cis*. On the other hand, the NOESY spectrum of **6** showed cross peaks between H_h (δ_H 7.37) and H_f (δ_H 2.26), H_i (δ_H 3.39) and H_j (δ_H 2.50), respectively, but not between H_h and H_g (δ_H 6.20) and H_i and H_f, thus indicating that the phenyl group is situated close to the pyrrolidinyl and methylene groups and *cis* to the methylsulfanyl group.



5 **6**

The formation of **3** and **4** indicates that the hydroxide nucleophile attacks selectively at the carbon bonded to the pyrrolidinyl group and the resulting pyrrolidinylcyclopropenes **2a,b** undergo ring-opening by the cleavage of the (*a*) and (*b*) bonds to give **3** and **4**, respectively. Recently we proposed that reactions with cyclopropenes can proceed *via* the formation of vinylcarbenes upon ring-opening.[3] On the basis of this mechanism, the conversion of **2a,b** into **3** and **4** is thought to proceed *via* the intermediary formation of vinylcarbenes **7** and **8**, respectively, in which the carbenic carbons are stabilized by the more electron-donating alkylsulfanyl groups, followed by the migration of the double bond and protonation, as shown in Scheme 2.



8 **2a, b** **7**

Scheme 2

Experimental

IR spectra were recorded on a Perkin-Elmer model 1600 FT spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 FT spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values

are in Hz. Mass spectra were obtained at 70 eV with a Finnigan mat TSQ 70 or Shimadzu LKB-9000 spectrometer. Elemental analyses were performed with a Yanaco CHN CORDER MT-3 and a Perkin-Elmer 2400 II CHNS/O analyser. Column chromatography was performed on silica gel (Wakogel C-300).

General procedures for reaction of pyrrolidinylcyclopropenyl cations 1a,b in alkaline aqueous solution

To a suspension of **1a,b** (0.58 mmol) in H_2O (10 cm^3) was added aqueous sodium hydroxide (10 cm^3, 1.74 mmol, 3 equiv.). The turbid solution was stirred at room temperature for 1 h, during which time an oily substance separated out. The mixture was extracted with CH_2Cl_2 (50 cm^3 × 2) and the combined extracts were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent to give **3** (85%) and **4** (82%), respectively.

(*Z*)-3-*tert*-Butylsulfanyl-2-methylsulfanyl-1-(pyrrolidin-1-yl)-prop-2-en-1-one 3. Pale yellow viscous liquid (Found: C, 55.4; H, 8.0; N, 5.2; S, 24.9. $C_{12}H_{21}NOS_2$ requires C, 55.55; H, 8.16; N, 5.40; S, 24.72%); ν_{max}/cm^{-1} (neat) 2963 2925, 2875, 1622 (C=O), 1551, 1414, 1367, 1339, 1251, 1224, 1163, 1072, 789, 736 and 703; δ_H 6.82 (1 H, s, olefin-H), 3.53 (4 H, m, pyrrolidinyl 2′,5′-H), 2.24 (3 H, s, SMe), 1.92 (4 H, m, pyrrolidinyl 3′,4′-H) and 1.41 (9 H, s, Bu^t); δ_C 16.71, 26.37, 26.43, 31.10, 44.93, 45.86, 48.41, 128.98, 149.56 and 165.51; *m/z* 259 (M^+).

(*E*)-3-Methylsulfanyl-2-phenyl-1-(pyrrolidin-1-yl)prop-2-en-1-one 4. Pale yellow viscous liquid (Found: C, 67.85; H, 6.9; N, 5.5; S, 13.2. $C_{14}H_{17}NOS$ requires C, 67.98; H, 6.93; N, 5.66; S, 12.96%); ν_{max}/cm^{-1} (neat) 3054, 2970, 2924, 2875, 1621 (C=O), 1493, 1416, 1336, 1294, 1250, 1226, 1189, 914, 774 and 699; δ_H 7.39 (5 H, m, phenyl-H), 6.85 (1 H, s, olefin-H), 3.53 and 3.00 (each 2 H, m, pyrrolidinyl 2′,5′-H), 2.37 (3 H, s, SMe) and 1.76 (4 H, m, pyrrolidinyl 3′,4′-H); δ_C 18.10, 24.19, 26.13, 46.22, 48.26, 127.53, 128.23, 128.42, 133.73, 135.29, 135.51 and 168.26.

General procedure for reduction by $LiAlH_4$

To a suspension of lithium aluminium hydride (1.85 mmol) in dry diethyl ether (10 cm^3) was added a solution of **3** or **4** (0.37 mmol) in dry diethyl ether (5 cm^3) under argon and the mixture was refluxed for 1.5 h. After the mixture was cooled to room temperature, ethyl acetate (25 cm^3) and aq. ammonium chloride (25 cm^3) were added. The mixture was extracted with diethyl ether (30 cm^3 × 2) and the combined extracts were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with diethyl ether as eluent to give **5** (68%) and **6** (71%), respectively.

(*Z*)-1-*tert*-Butylsulfanyl-2-methylsulfanyl-3-(pyrrolidin-1-yl)-prop-1-ene 5. Pale yellow viscous liquid (Found: C, 58.6; H, 9.1; N, 5.9. $C_{12}H_{23}NS_2$ requires C, 58.87; H, 9.39; N, 5.71%); ν_{max}/cm^{-1} (neat) 2961, 2924, 2874, 2785, 1568, 1471, 1456, 1436, 1392, 1365, 1345, 1319, 1287, 1162, 1123, 877 and 835; δ_H 6.37 (1 H, s, olefin-H), 3.27 (2 H, s, CH_2), 2.51 (4 H, m, pyrrolidinyl 2′,5′-H), 2.36 (3 H, s, SMe), 1.78 (4 H, m, pyrrolidinyl 3′,4′-H) and 1.39 (9 H, s, Bu^t); δ_C 14.67, 23.64, 31.14, 44.36, 53.66, 61.34, 122.43 and 132.29; *m/z* 245 (M^+).

(*E*)-1-Methylsulfanyl-2-phenyl-3-(pyrrolidin-1-yl)prop-1-ene 6. Pale yellow viscous liquid (Found: C, 72.2; H, 8.0; N, 5.8. $C_{14}H_{19}NS$ requires C, 72.05; H, 8.21; N, 6.00%); ν_{max}/cm^{-1} (neat) 3055, 3020, 2963, 2921, 2873, 2785, 1646, 1599, 1492, 1458, 1441, 1373, 1346, 1316, 1290, 1124, 1027, 878, 833, 765 and 698; δ_H 7.37 (5 H, m, phenyl-H), 6.20 (1 H, s, olefin-H), 3.39 (2 H, s, CH_2), 2.50 (4 H, m, pyrrolidinyl 2′,5′-H), 2.26 (3 H, s, SMe) and 1.74 (4 H, m, pyrrolidinyl 3′,4′-H); δ_C 17.93, 23.48, 23.56, 30.34, 54.13, 63.08, 127.08, 127.20, 127.97, 128.11, 135.51 and 139.63.

References

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