Reaction of Diphenylcyclopropenone with Primary and Secondary Enaminones. Synthetic and Mechanistic Implications

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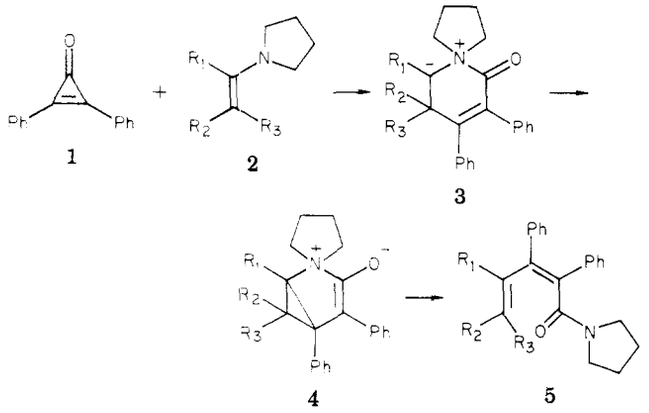
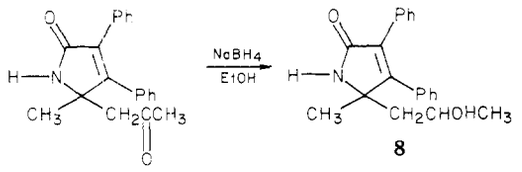
Diphenylcyclopropenone (1) reacts with the primary and secondary acyclic enaminones **6a–c** in toluene at reflux to afford the 1,5-dihydro-2*H*-pyrrol-2-ones **7a–c** in good yield. The reaction of the primary cyclic enaminone **13a** produces a 1,5-dihydro-4*H*-pyrrol-4-one **14**, while the secondary cyclic enaminone **13b** yields a 2:1 product (**16b**) as the principal cycloadduct. Mechanisms are discussed.

The reaction of diphenylcyclopropenone (1) with a variety of enamines (2) has been suggested to proceed through ylide (3) and ammonium enolate (4) intermediates to afford the C–N insertion products (5).[1] Stable examples



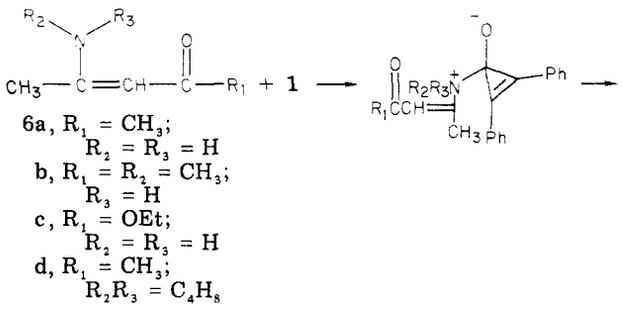
of 4 have been reported.[2] Intermediates analogous to 3 and 4 have been proposed in the reaction of tertiary enaminones (2, R_2 = COR) with 1, where C–N insertion products are also observed.[3] Although primary and secondary enaminones have long been known,[4] the utilization of these systems as mechanistic probes in the above reaction, where rapid proton transfer in intermediates might permit the isolation of interesting heterocycles, has not been explored.

We began our study with the acyclic enaminones **6a–c** for which a smooth reaction with 1 was observed in toluene under reflux conditions (3 days), affording the 1,5-dihydro-2*H*-pyrrol-2-ones **7a** (76%), **7b** (66%), and **7c** (77%), respectively (Scheme I, Table I). Evidence for the structural assignments was obtained from the spectral data. The IR spectrum of **7a**, for example, showed ketone C=O (1725 cm^{-1}) and amide NH (3320 cm^{-1}) and C=O (1700 cm^{-1}). The NMR spectrum of **7a** contained an AB quartet at δ 2.8 (J = 17 Hz). Sodium borohydride reduction of **7a** produced the diastereomeric alcohols **8**, the IR spectrum of which showed a single carbonyl absorption at 1690 cm^{-1}.[5] These results permit an alternative rep-

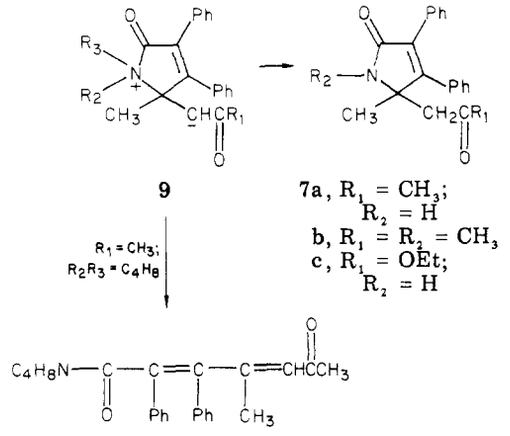


7a

Scheme I



6a, R_1 = CH_3; R_2 = R_3 = H
b, R_1 = R_2 = CH_3; R_3 = H
c, R_1 = OEt; R_2 = R_3 = H
d, R_1 = CH_3; R_2R_3 = C_4H_8



9

7a, R_1 = CH_3; R_2 = H
b, R_1 = R_2 = CH_3
c, R_1 = OEt; R_2 = H

R_1 = CH_3; R_2R_3 = C_4H_8

10

resentation (Scheme I) of the reaction of 1 with acyclic enaminones as a cycloaddition at NC_β of the enaminone to afford intermediate **9**, which could also account for the formation of the previously reported[3] C–N insertion products **10** obtained from tertiary enaminones. Under our conditions the reaction of **6d** formed **10** in 38% yield.

The reaction of **6b** gave a small amount (10%) of a 2:1 adduct which was assigned structure **11** on the basis of IR absorptions at 1755 and 1645 cm^{-1}, the latter suggesting a 1,5-dihydro-4*H*-pyrrol-4-one structure.[6] The formation of **11** is consistent with the participation of an imine intermediate **12** resulting from initial nucleophilic attack of the enaminone oxygen at C-1 of **1**.[7] Imines have been

(1) V. Bilinski, M. A. Steinfels, and A. S. Dreiding, *Helv. Chim. Acta*, **55**, 1075 (1972).
(2) T. Eicher and S. Bohm, *Tetrahedron Lett.*, 2603 (1972).
(3) V. Bilinski and A. S. Dreiding, *Helv. Chim. Acta*, **57**, 2525 (1974).
(4) J. V. Greenhill, *Chem. Soc. Rev.*, **6**, 277 (1977).

(5) An unusual feature in the NMR spectrum of **7a** is the presence of the amide NH at δ 2.0. Examination of a model indicates a favorable conformation for **7a** in which the ketone C=O is situated above this hydrogen. In any case, the reduction product **8** shows the amide NH at δ 7.85.

(6) T. Eicher, J. L. Weber, and G. Chatila, *Justus Liebigs Ann. Chem.*, 1203 (1978).

(7) An analogous lactone structure has been proposed for the dimer of **1**: R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

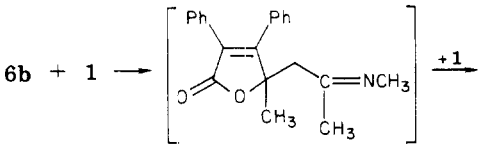
0022-3263/80/1945-5340$01.00/0

Table I. Products from the Reaction of 1 with Enaminones in Toluene at Reflux

enaminone	reaction time, days	1:1 adduct (% yield, mp °C)	2:1 adduct (% yield, mp, °C)	PhC≡CPh, % yield
6a	3	7a (76, 171-172)		7
6b	3	7b (66, 85-87)	11 (10, 233-236)	5
6c	3	7c (77, 120-120.5)		6
6d	3	10 (38, 167-168.5[a])		5
13a	7	14 (43, 258-259)	16a (5, 243-246)	16
13b	7	18 (14, 129.5-130)	16b (25, 256.5-257)	36
13c	7			57[b]

[a] Melting point is of the major isomer.[3] [b] In addition, 37% 1 and 78% 13c were recovered.

shown to react with 1 to afford 1,5-dihydro-4*H*-pyrrol-4-ones.[6]



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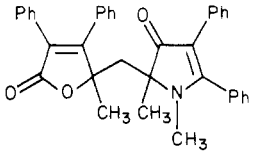

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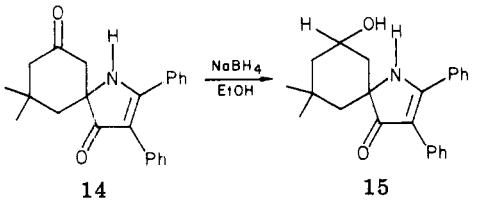
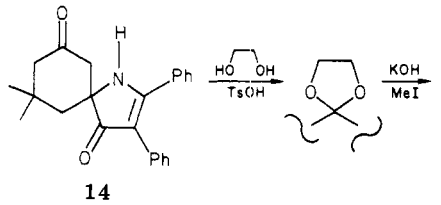
The cyclic enaminones **13a–c** proved to be much less reactive. In the case of **13c**, which was the least reactive, a 7-day reaction afforded only diphenylacetylene (57%) in addition to unreacted 1 (37%) and **13c** (78%). The principal product of the reaction of **13a**, a 1:1 adduct, was assigned the 1,5-dihydro-4*H*-pyrrol-4-one structure **14** (Scheme II, Table I) on the basis of the IR spectrum which showed absorptions at 3165 (NH), 1720 (C=O), and 1635 (N—C=C—C=O). Sodium borohydride reduction of **14** gave the diastereomeric alcohols **15** (IR 3330, 3220, 1640

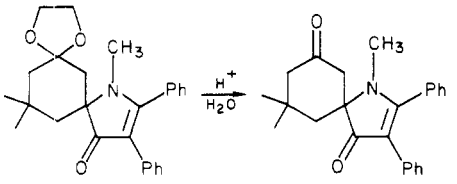


14 15

cm^{-1}). A small amount of 2:1 adduct **16a** (5%) was also obtained. In the case of **13b**, the 2:1 product (**16b**) was the principal cycloadduct. A 1:1 adduct was also isolated, but could not be assigned as a pyrrol-2-one or -4-one by spectroscopic means alone (carbonyl at 1665 cm^{-1}). Therefore, N-methylation of **14** was performed according to the sequence shown below. The product **17** (N—C=

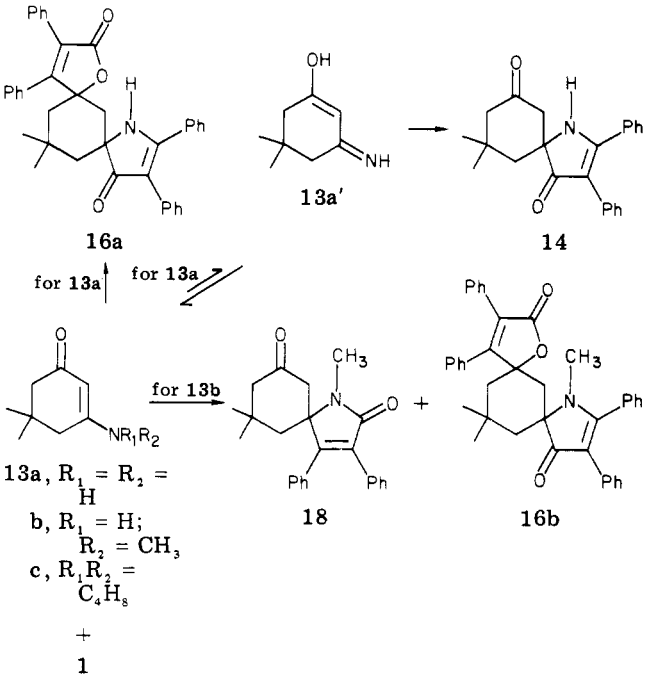


14



17

Scheme II



16a 13a′ 14

13a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1R_2 = C_4H_8$
+
1

18 16b

C—C=O, 1645 cm^{-1}) proved to be isomeric with that of the reaction of **13b**, thereby defining the latter as the 1,5-dihydro-2*H*-pyrrol-2-one **18**. Thus, of the 1:1 adducts isolated in this study, **14** was the only 1,5-dihydro-4*H*-pyrrol-4-one observed. The difference here is consistent with reaction of **13a** through an imino tautomer, i.e., **13a′**, a form generally considered to make little contribution to the structure of enaminones.[4] It is interesting to note that primary cyclic enaminones show a weak absorption in their IR spectra at 1650–1690 cm^{-1}, which is absent in those of the secondary and tertiary derivatives.[8]

A difference in reactivity for cyclic vs. acyclic enaminones has been observed previously[4] and should be related to the existence of the former in a fixed trans-s-trans form. Increased electron delocalization from N to O has been suggested for this case,[9] which is consistent with the observed greater participation of a pathway involving reaction of 1 at the oxygen of cyclic enaminones. The failure of **13c** to afford a product of reaction at oxygen suggests that proton transfer from nitrogen, in an intermediate or transition state, plays an important role in preventing reversibility of the process.

The reaction described here provides a convenient route to 5-functionalized 1,5-dihydro-2*H*-pyrrol-2-ones, a process

(8) K. Ramalingam, M. Balasubramanian, and V. Baliah, *Indian J. Chem.*, 10, 62 (1972).
(9) D. Smith and P. J. Taylor, *Spectrochim. Acta, Part A*, 32, 1477 (1976).

which appears to be particularly favorable when applied to acyclic enaminones. The resulting systems may find utility as intermediates in the synthesis of more complex heterocycles.

Experimental Section

The melting points are uncorrected. The IR spectra of KBr disks were measured with a Perkin-Elmer 337 spectrophotometer, NMR spectra (in $CDCl_3$, unless otherwise stated) with a Varian T-60 instrument with Me_4Si as an internal standard, and mass spectra with a Varian MAT 311A spectrometer (unless otherwise indicated).

The enaminones[4] and diphenylcyclopropenone[7] were prepared according to known procedures.

Reaction of Enaminones 6a-d with Diphenylcyclopropenone (1). In a typical reaction, a solution of **1** (2 mmol) and **6** (2 mmol) in toluene (10 mL) was heated at reflux for 3 days after which time the solvent was evaporated. The crude reaction mixture was treated as follows.

A. Reaction of 6a. Trituration with ethyl ether gave 71% of the insoluble 1,5-dihydro-2*H*-pyrrol-2-one **7a**: NMR δ 1.55 (s, 3 H), 2.0 (s, 1 H, NH), 2.15 (s, 3 H), 2.8 (AB, 2 H, J = 17 Hz), 7.15–7.6 (m, 10 H); IR 3320, 1725, 1700 cm^{-1}; mass spectrum, m/e (relative intensity) 305 (42), 249 (17), 248 (100), 178 (16).

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.83; H, 6.15; N, 4.63.

Chromatography of the soluble material on silica gel afforded 7% diphenylacetylene (eluted with benzene, identical in all respects with an authentic sample) and **7a** (5%; with 10% ethyl ether–benzene).

B. Reaction of 6b. Chromatography of the residue on silica gel with benzene as eluant afforded diphenylacetylene (5%) and with 2% ethyl ether–benzene afforded the 2:1 adduct **11** (10%): NMR δ 1.45 (s, 3 H), 1.6 (s, 3 H), 2.05 (d, 1 H, J = 15 Hz), 2.75 (d, 1 H, J = 15 Hz), 3.1 (s, 3 H), 7.1–7.6 (m, 20 H); IR 1755, 1645 cm^{-1}; mass spectrum, m/e (relative intensity) 525 (100), 276 (15), 263 (25), 262 (35), 178 (31).

Anal. Calcd for $C_{36}H_{31}NO_3$: C, 82.26; H, 5.94; N, 2.66. Found: C, 82.41; H, 6.02; N, 2.55.

Elution with 10% ethyl ether–benzene gave the 1,5-dihydro-2*H*-pyrrol-2-one **7b** (66%): NMR δ 1.45 (s, 3 H), 2.1 (s, 3 H), 2.85 (AB, 2 H, J = 16 Hz), 3.05 (s, 3 H), 7.15–7.6 (m, 10 H); IR 1720, 1680 cm^{-1}; mass spectrum, m/e (relative intensity) 319 (30), 263 (19), 262 (100), 178 (5).

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 78.88; H, 6.55; N, 4.25.

C. Reaction of 6c. Trituration with ethyl ether afforded 67% of the 1,5-dihydro-2*H*-pyrrol-2-one **7c** which was recrystallized with methylene chloride–hexane: NMR δ 1.25 (t, 3 H, J = 7 Hz), 1.55 (s, 3 H), 2.7 (s, 2 H), 4.25 (q, 2 H, J = 7 Hz), 7.15–7.65 (m, 11 H) (10 H, D_2O); IR 3165, 3060, 1730, 1695 cm^{-1}; mass spectrum, m/e (relative intensity) 335 (39), 249 (18), 178 (14).

Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.33; H, 6.28; N, 4.25.

Chromatography of soluble part on silica gel gave diphenylcyclopropenone (6%, elution with benzene) and **7c** (10%, elution with 10% ethyl ether–benzene).

D. Reaction of 6d. Chromatography on silica gel gave several fractions of a mixture of the two 1:1 insertion products **10**[3] (14%, eluted with 5% ethyl ether-benzene) and several fractions of one component of this mixture (24%): mp 167–168.5 °C; NMR δ 1.83 (m, 4 H), 2.1 (d, 3 H, J = 1.5 Hz), 2.25 (s, 3 H), 3.2–3.75 (2 overlapping t, 4 H), 6.45 (br s, 1 H), 7.1–7.4 (m, 10 H); IR 1690, 1620 cm^{-1}; mass spectrum, m/e (relative intensity) 359 (2), 316 (100), 261 (32).

Reaction of Enaminones 13a–c with Diphenylcyclopropenone (1). The general procedure was the same as above except that the reaction time was 7 days. After evaporation of toluene the crude residue was treated as follows.

A. Reaction of 13a. Trituration with ethyl ether afforded 43% of the 1,5-dihydro-4*H*-pyrrol-4-one **14** which was recrystallized with methylene chloride–hexane: NMR δ 1.1 (s, 6 H), 1.4–2.7 (m, 5 H), 2.9 (d, 1 H, J = 17 Hz), 5.5 (br s, 1 H), 7.3 (s, 5 H), 7.5 (s, 5 H); IR 3165, 1720, 1635 cm^{-1}; mass spectrum, m/e (relative intensity) 345 (63), 178 (100).

Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 80.16; H, 6.86; N, 3.98.

Chromatography with silica gel afforded diphenylacetylene (16%, elution with benzene) and the 2:1 adduct **16a** (5%, elution with benzene) which was recrystallized with methylene chloride–hexane: NMR δ 1.1 (s, 3 H), 1.5 (s, 3 H), 1.6–2.0 (m, 5 H), 2.45 (d, 1 H, J = 14 Hz), 6.55 (s, 1 H), 7.15–7.6 (m, 20 H); IR 3400, 1760, 1665 cm^{-1}; mass spectrum, m/e (relative intensity) 551 (100), 178 (70).

Anal. Calcd for $C_{38}H_{33}NO_3$: C, 82.73; H, 6.03; N, 2.54. Found: C, 82.54; H, 6.14; N, 2.61.

B. Reaction of 13b. Chromatography of the residue on silica gel with benzene as eluant afforded diphenylacetylene (36%) and the 2:1 adduct **16b** (25%) which was recrystallized with methylene chloride–hexane: NMR δ 1.2 (s, 3 H), 1.4 (s, 3 H), 1.55–2.45 (m, 5 H), 2.65 (d, 1 H, J = 15 Hz), 3.1 (s, 3 H), 7.1 (s, 5 H), 7.15–7.6 (m, 15 H); IR 1760, 1650 cm^{-1}; mass spectrum, m/e (relative intensity) 565 (100), 178 (93).

Anal. Calcd for $C_{39}H_{35}NO_3$: C, 82.81; H, 6.24; N, 2.48. Found: C, 83.02; H, 6.15; N, 2.59.

Elution with 2% ethyl ether–benzene afforded the 1,5-dihydro-2*H*-pyrrol-2-one **18** which was recrystallized from cold ispropyl ether: NMR δ 1.25 (s, 3 H), 1.3 (s, 3 H), 1.7–2.7 (m, 5 H), 2.9 (d, 1 H, J = 17 Hz), 2.95 (s, 3 H), 7.25 (s, 5 H), 7.3–7.6 (m, 5 H); IR 1715, 1665 cm^{-1}; mass spectrum, m/e (relative intensity) 359 (61), 178 (100).

Anal. Calcd for $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90. Found: C, 80.00; H, 7.13; N, 4.08.

C. Reaction of 13c. Chromatography of the residue with silica gel afforded diphenylacetylene (57%, elution with benzene), unreacted diphenylcyclopropenone (37%, elution with 5% ethyl ether–benzene), and unreacted enaminone **13c** (78%, 3% methanol–ethyl ether).

Reduction of 7a with Sodium Borohydride. To an ethanol solution (10 mL) of **7a** (100 mg, 0.33 mmol) was added sodium borohydride (40 mg, 1.1 mmol). After 17 h, the solvent was evaporated and the solid residue treated with 10% ammonium chloride (6 mL). The methylene chloride extract (3 × 10 mL) was dried ($MgSO_4$) and evaporated, yielding 94 mg (93%) of the diastereomers **8**; IR 3400, 3200, 1690 cm^{-1}. One isomer was obtained pure by recrystallization from methylene chloride–hexane: mp 175–177 °C; NMR δ 1.25 (d, 3 H, J = 6.5 Hz), 1.5 (s, 3 H), 1.7–2.1 (m, 2 H), 4.15 (br s, 2 H, OH, CH), 7.1–7.5 (m, 10 H), 7.85 (br s, 1 H, NH); IR 3425, 3180, 1690; mass spectrum, m/e (relative intensity) 307 (31), 249 (25), 248 (100), 179 (10), 178 (15).

Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.26; H, 6.73; N, 4.62.

Reduction of 14 with Sodium Borohydride. A suspension of **14** (256 mg, 0.742 mmol) and sodium borohydride (52 mg, 1.37 mmol) in ethanol (25 mL) was left at room temperature with stirring for 17 h after which time the solvent was evaporated and 10% ammonium chloride (10 mL) added to the residue. The solid product was filtered, washed with water, and air-dried, yielding 250 mg (97%) of the diastereomers **15**: mp 102-120 °C; IR 3330, 3220, 1640 cm^{-1}; NMR δ 0.95 (s, 3 H), 1.3 (s, 3 H), 1.5–1.85 (m, 6 H), 2.2 (br, 1 H), 4.3 (m, 1 H), 6.8 (br, 1 H), 7.2–7.5 (m, 10 H).

Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03. Found: C, 79.68; H, 7.41; N, 4.17.

N-Methylation of 14 via Ketal. A. A solution of **14** (165 mg, 0.478 mmol), ethylene glycol (0.03 mL, 0.05 mmol), *p*-toluenesulfonic acid (10 mg), and benzene (3 mL) was left at reflux for 5 h with the reaction flask connected to a Dean–Stark trap. The reaction mixture was cooled, washed with a 10% sodium hydroxide solution (2 × 6 mL), followed by distilled water (2 × 6 mL), dried over anhydrous potassium carbonate, and filtered, and the solvent was evaporated, yielding 171 mg (92%) of crude ketal, IR 3370, 1670 cm^{-1}, which was used directly in the next step.

B. To a suspension of the ketal formed above (155 mg, 0.399 mmol) in dimethyl sulfoxide (2 mL) was added approximately 150 mg of powdered potassium hydroxide. All of the ketal then dissolved and the solution turned dark orange. Methyl iodide (0.14 mL, 2.2 mmol) was added and the reaction mixture was left stirring for 0.5 h. Water (20 mL) was then added to the yellow reaction mixture and the product extracted with methylene chloride (3 × 20 mL). The organic layer was washed with water (6 × 20 mL), dried over anhydrous potassium carbonate, and

filtered, and the solvent was evaporated, yielding 152 mg of crude product. Trituration with hexane afforded the methylated ketal (70 mg, 44%): mp 132–140 °C; NMR δ 1.15 (s, 3 H), 1.20 (s, 3 H), 1.25–2.0 (m, 5 H), 2.35 (d, 1 H, J = 16 Hz), 3.05 (s, 3 H), 3.9–4.05 (m, 4 H), 7.05 (s, 5 H), 7.2–7.6 (m, 5 H); IR 1670 cm^{-1}.

C. A solution of the methylated ketal (70 mg, 0.17 mmol), 6 N hydrochloric acid (1 mL), and ethanol (3 mL) was left at room temperature for 10 h. The solvent was evaporated, water was added to the residue (15 mL), and the product was extracted with methylene chloride (2 × 20 mL). The organic layer was then washed with water (3 × 15 mL), dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated, yielding 56 mg of crude product which was recrystallized with isopropyl ether (left in freezer), affording 41 mg (67%) of pure 17: mp 147.5–148 °C; NMR (CCl_4) 1.15 (s, 3 H), 1.20 (s, 3 H), 1.6–2.55 (m, 5 H), 2.80 (d, 1 H, J = 17 Hz), 2.85 (s, 3 H), 7.1 (s, 5 H), 7.25–7.6 (m, 5 H); IR 1720, 1640 cm^{-1}; mass spectrum (Finnigan 1015 S/L), m/e (relative intensity) 359 (2), 246 (10), 178 (100).

Anal. Calcd for $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90. Found: C, 80.08; H, 6.93; N, 4.01.

Registry No. 1, 886-38-4; **6a**, 1118-66-7; **6b**, 14092-14-9; **6c**, 7318-00-5; **6d**, 3389-57-9; **7a**, 75476-11-8; **7b**, 75476-12-9; **7c**, 75476-13-0; 8 (isomer 1), 75476-14-1; 8 (isomer 2), 75476-15-2; **10**, 75476-16-3; **11**, 75495-03-3; **13a**, 873-95-0; **13b**, 701-58-6; **13c**, 3357-16-2; **14**, 75495-04-4; **14**·ethylene ketal, 75476-21-0; **15** (isomer 1), 75476-17-4; **15** (isomer 2), 75476-23-2; **16a**, 75495-05-5; **16b**, 75476-18-5; **17**, 75476-19-6; **17**·ethylene ketal, 75476-22-1; **18**, 75476-20-9.

Crystal and Molecular Structure of Di-*tert*-adamantyl Disulfide. Extension of the Correlation between the Sulfur–Sulfur Dihedral Angle and the Sulfur Lone-Pair Energy Gap[1]

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The crystal and molecular structure of di-*tert*-adamantyl disulfide (1, DAD; $C_{20}H_{30}S_2$) has been determined from diffractometer data. The unit cell is monoclinic: space group $P2_1/c$; a = 12.015 (3), b = 11.556 (3), c = 12.959 (3) Å; β = 90.42 (2)°; V = 1799 Å^3; Z = 4; d_{calcd} = 1.24 Mg/m^{-3}. Least-squares refinements gave R = 0.074 for 649 observed reflections. The torsion angle θ(CSSC) = 110.5 (9)°. The observation of an enlarged S–S dihedral angle permits a tentative extension of the correlation between θ(CSSC) and the photoelectron spectroscopically determined ionization energy difference, $\Delta E(n_+-n_-)$, and disulfide torsional angles above 90°. The molecular geometry of t-Bu–SS–t-Bu is revised accordingly.

Dialkyl disulfides represent a class of substances both intensely studied in the laboratory[2] and widely distributed in nature.[3] A singular structural feature of the disulfide moiety is its S–S dihedral angle of 80–85° in an unstrained molecular environment.[4] Deviations of up to 70° to smaller values of θ(CSSC) have been forced on the system by the expediency of ring formation. Although the unsubstituted parent, H_2S_2, enjoys an S–S torsional angle of 91°,[5] very few other examples with expanded θ(CSSC)'s are known. Notable exceptions are cysteine derivatives either strongly hydrogen bonded in the solid phase[6,7] or rigidly held in a protein.[8] Very recently a dipyrimidyl disulfide was found to sustain θ(CSSC) = 180° via the agency of copper complexation.[9]

Table I. Crystal Data for DAD

formula	$C_{20}H_{30}S_2$	V	1799.13 Å^3
fw	334.59	Z	4
space group	$P2_1/c$	temp	295 K
a	12.015 (3) Å	μ (Mo Kα)	0.62 mm^{-1}
b	11.556 (3) Å	d_{calcd}	Mg m^{-3}
c	12.959 (3) Å	cryst dimens	0.80 × 0.10 × 0.20 mm
β	90.4 (2)°		

Absent from the rich chemistry of the disulfide functionality is a series of simple derivatives with S–S dihedral angles spanning the 90–180° range. As part of a program designed to prepare and study these substrates, we have undertaken the X-ray structure determination of t-Ad–SS–t-Ad (DAD, 1). The results presented below confirm our molecular mechanics predictions of θ(CSSC) enlargement by means of bulky substituents[1b,10] and provide us with an opportunity to extend the θ(CSSC)/$\Delta E(n_+-n_-)$ correlation beyond 90°.

(1) Organo-Sulfur Mechanisms. 12. (a) Part 11, J. P. Snyder and T. A. Halgren, *J. Am. Chem. Soc.*, **102**, 2861 (1980); (b) part 10, F. S. Jørgensen and J. P. Snyder, *J. Org. Chem.*, **45**, 1015 (1980).

(2) (a) *Org. Comp. Sulfur, Selenium, Tellurium*, 1 (1970); 2 (1973); 3 (1975); E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978; (b) A. Senning, Ed., "Sulfur in Organic and Inorganic Chemistry", Marcel Dekker, New York, Vol. 1, 2 (1971); Vol. 3 (1972).

(3) A. Kjaer, *Pure Appl. Chem.*, **49**, 137 (1977); D. J. Faulkner, *Tetrahedron*, **33**, 1421 (1977); B. Granroth, *Ann. Acad. Sci. Fenn., Ser. A2*, **No. 154**, 6 (1970); M. H. Brodnitz, J. V. Pascale, and L. V. Derslice, *J. Agric. Food Chem.*, **19**, 273 (1971); M. H. Brodnitz, C. L. Pollock, and P. P. Vallon, *ibid.*, **17**, 760 (1969).

(4) P. H. Laur, ref 2b, 1972, Vol. 3, p 91.

(5) G. Winnewisser, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, **49**, 3465 (1968).

(6) H. L. Yakel and E. W. Hughes, *Acta Crystallogr.*, **7**, 291 (1954); B. M. Oughton and P. M. Harrison, *ibid.*, **12**, 396 (1959).

(7) R. E. Rosenfield, Jr., and R. Parthasarathy, *Acta Crystallogr., Sect. B*, **B31**, 462 (1975).

(8) U. Ludescher and R. Schwyzer, *Helv. Chim. Acta*, **54**, 1637 (1971); H. E. van Wart and H. A. Scheraga, *J. Phys. Chem.*, **80**, 1823 (1976); cf. Figure 3 and references therein.

(9) C. J. Simmons, M. Lundeen, and K. Seff, *J. Chem. Soc., Chem. Commun.*, 595 (1979); *Inorg Chem.*, **18**, 3444 (1979).

(10) F. S. Jørgensen and J. P. Snyder, *Tetrahedron*, **35**, 1399 (1979).

0022-3263/80/1945-5343$01.00/0