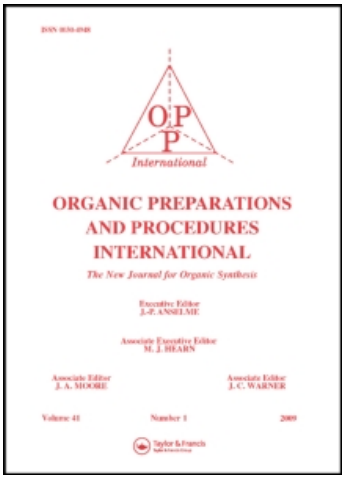

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[2+2] CYCLOADDITION REACTIONS OF ENAMINES WITH ELECTRON-DEFICIENT ACETYLENES

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[2+2] CYCLOADDITION REACTIONS OF ENAMINES WITH ELECTRON-DEFICIENT ACETYLENES

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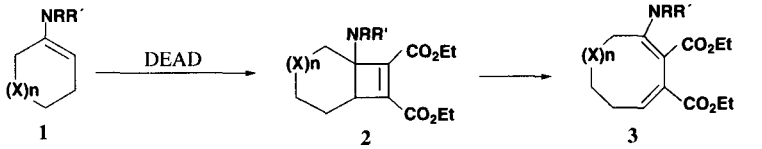
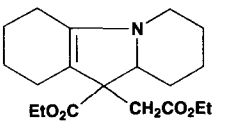
[2+2] Cycloaddition reactions have become important in synthethic organic chemistry[1] and are usually performed in nonpolar solvents. Enamines derived from cyclic ketones, undergo cycloaddition reactions to yield cyclobutene derivatives which then isomerize to 1,3-dienamines with expansion of the ring. However, when polar solvents such as methanol or acetonitrile are used, the reaction of a pyrrolidine enamine with dimethyl acetylenedicarboxylate (DMAD) behaves differently to yield a pyrrolizine derivative (e. g. **4**).[2] Not only does the polarity of the solvent affect the course of the reaction, but both the structure of the enamines and type of acetylenes may also alter the course of the reaction. Herein we report the cycloaddition of enamines of cyclopentanone and cyclohexanone (**1a-f**) with diethyl acetylenedicarboxylate (DEAD) and cycloaddition of α-tetralone enamines (**5a-c**) with DMAD in two different solvents, benzene and methanol, respectively.[3] The cycloaddition of butanal enamines (**7a-c**) with DMAD was also investigated.



1 2 3

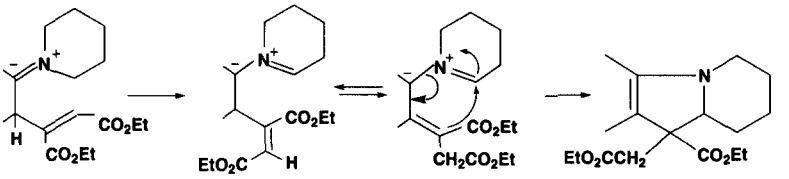
a) n= 1, NRR'= morpholine b) n= 1, NRR'= pyrrolidine
c) n= 1, NRR'= piperidine d) n= 0, NRR'= morpholine
e) n= 0, NRR'= pyrrolidine f) n= 0, NRR'= piperidine



4

1-(N-Morpholinyl)cyclohexene (**1a**) was converted directly to the ring-opened cycloisomerization product (**3a**) in one step when allowed to react with DEAD at 5-7° either in benzene and methanol. A similar result was observed with 1-(N-pyrrolidinyl)cyclohexene (**1b**) in methanol and **3b** is obtained in one step; however, in benzene the [2+2] cyclobutene adduct (**2b**) could be isolated. When **2b** was heated at 80° for 6 hours, the same cycloisomerization product (**3b**) was obtained. 1-(N-Piperidinyl)cyclohexene (**1c**) behaved in a similar manner to 1-(N-pyrrolidinyl)cyclohexene in

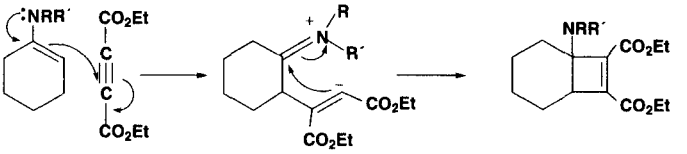
benzene solution but a new product, **4** was formed in methanol, probably via a mechanism similar to the formation of pyrrolizines. In literature, pyrrolizine derivatives were obtained either by reaction of pyrrolidinyl enamines (e. g. **1b** and **1e**) with DMAD in protic polar solvents,[2d] or by the smooth conversion of 1-(N- pyrrolidinyl)cyclobutenes (e. g. **2b** and **2e**).[4]



Initial nucleophilic addition of the enamine to the acetylene triple bond leads to dipolar intermediate (**a**); the intramolecular abstraction of one of the α–methylene protons of the piperidinium group by the carbanionic centre then, results in the formation of a 1,3-dipole (**b**). After a second proton transfer the 1,3-dipole is extended to a 1,5-dipole system (**c**), a symmetry-allowed disrotatory 1,5-dipolar cyclization occurs to give **d**.

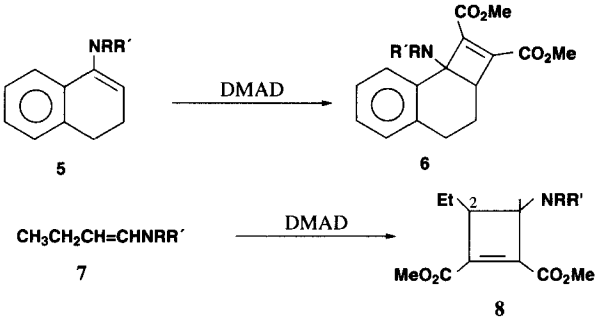
The structures of the cycloaddition and cycloisomerization products were assigned on the basis of their NMR spectra. The characteristic peak of the bridgehead proton of cycloadducts was present as broad multiplet at 3.8-4.6 ppm and no vinyl protons were evident in the NMR spectra. A characteristic absorption of the cycloisomerization products at around δ 6.7-6.9 (a doublet-doublet) for vinylic proton could be detected. There is not a good correlation between the nucleophilic effect of the secondary amine group and the chemical shift in the NMR resonance of the vinylic proton in cyclooctadiene structures. X-ray structure determinations of similar compounds show that not much conjugation is present in 1,3- diene moiety.[4]

The more effective p-electron donating pyrrolidine and piperidine groups, in contrast to morpholine enhance the nucleophilicity of the enamine double bond thus favoring the formation of the cyclobutene adduct in [2+2] cycloaddition reactions.



The direct conversion of 1-(N-morpholinyl)cyclohexene and 1-(N-pyrrolidinyl)cyclohexene with DEAD to the corresponding cycloisomerization products can be attributed to stabilization of the 1,4-dipolar intermediates in polar protic solvents. In addition, the electrophilicity of DEAD is lower than that of DMAD which accounts for the lower reactivity of DEAD. Cyclopentanone enamines of morpholine, pyrrolidine and piperidine were also allowed to react with DEAD to give similar cycloisomerization products but the yields were lower. The yields are given in Table 1. α-Tetralone enamines (**5a-c**) were allowed to react with DMAD. Higher temperatures and longer reaction times

afforded cyclobutene adducts (**6a-c**) but no trace of ring opened products could be detected. Compound **6a** was obtained as an oil and could be crystallized after column chromotography but the cycloadducts **6b** and **6c** remained as oils. Because the double bond of butanal enamines (**7a-c**) are less nucleophilic, [2+2] cycloadditions with DMAD required more vigorous reaction conditions. The characteristic peaks for protons **1** and **2** in the NMR of the cycloadducts **8a-c** are shifted due to the type of cyclic amine attached.



a) NRR´ = morpholine b) NRR´ = pyrrolidine c) NRR´ = piperidine

The nucleophilic effect of cyclic amines decreases in the order: pyrrolidine > piperidine > morpholine. The pyrrolidine group in **8b** increases the electron density most effectively and the NMR peaks of both the H_1 and H_2 protons appear at higher fields (δ 4.5 and 5.75) while the H_1 and H_2 peaks of compound **8c** are at lower fields (δ 4.75 and 5.85) since the morpholino group has the lowest nucleophilic effect; thus H_1 and H_2 protons of compound **8a** appear at δ 4.85 and 5.90, respectively.

TABLE 1. Yields, mps and UV Data of Compounds **2-8**

Compd	mp. (°C)	λ_{max} [nm][a]	Yield (%)	Compd	mp. (°C)	λ_{max} [nm][a]	Yield (%)
2b	75	321, 245	58	**4**	oil	373	40
2c	41	—	56	**6a**	110	248	46
3a	154	327, 239	56	**6b**	oil	295, 250	54
3b	97	289, 243	48	**6c**	oil	252	47
3c	99	332, 241	49	**8a**	oil	284	56
3d	103	—	46	**8b**	oil	291	43
3e	114	307, 241	40	**8c**	oil	286	48
3f	96	341, 241	43				

a) In methanol

EXPERIMENTAL SECTION

All reactions were performed under an atmosphere of nitrogen. All solvents were carefully purified and dried by standard methods.[5] IR spectra were obtained on a Hitachi 270-30 spectrometer; absorp-

tion maxima were reported in wavenumbers (cm^{-1}). ^1H NMR spectra were recorded on either a Varian FT-80 A spectrometer or a WH-200 spectrometer; $CDCl_3$ was the solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts are reported in ppm (δ) downfield from the signal of TMS. The symbols, s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet), are used to report the multiplicity of signals. GCMS spectra were recorded on 5890 Series 2 Gas Chromotography, 5971 Series Mass Selective Detector Combine System and gave a parent peak and other fragmentations in agreement with the proposed structures. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected.

The morpholine, pyrrolidine and piperidine enamines of cyclohexanone, cyclopentanone, α-tetralone and butanal (**1a-f**, **5a-c** and **7a-c**) were prepared according to the literature procedures.[6-10]

General Procedure for the Reaction of Enamines (1a-c) with DEAD.- A solution of DEAD (5.46 mmol, 0.8 mL) in 15 mL benzene was added over a period of 2 h to a solution of **1a-c** (5.46 mmol) in 10 mL benzene at 5-7°. The reaction mixture was stirred for 6 or 7 h and then the solvent was removed under reduced pressure.

All reactions were repeated using methanol as solvent.

Diethyl 8-(N-Morpholinyl)-2,8-cyclooctadiene-1,2-dicarboxylate (3a).- Column chromatography of the residue [silica gel, benzene- ethyl acetate (4:1)] afforded pure **3a**. MS (70 ev): 337 (M^+); IR (KBr): 1710 and 1680 (ester C=O), 1600 (C=C) cm^{-1}; ^1H NMR: δ 6.6-6.75 (d-d, 1H, CH=C), 4.0-4.75 (m, 4H, CO_2CH_2), 3.6-3.85 (m, 4H, NCH_2), 3.5-3.75 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.55-2.75 (m, 8H, $CH_2CH_2CH_2CH_2$), 1.2-1.35 (t, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{18}H_{27}NO_5$: C, 64.09; H, 8.01. Found: C, 64.11; H, 7.96

Diethyl 1-(N-Pyrrolidinyl) bicyclo[4.2.0]octene-7,8-dicarboxylate (2b) could be isolated when **1b** was allowed to react similarly with DEAD in benzene solution. The partly crystalline residue was recrystallized from diethyl ether to give pure **2b**. MS (70 ev) : 321 (M^+); IR (KBr): 1720 and 1680 (ester C=O), 1620 (C=C) cm^{-1}; ^1H NMR: δ 4.35-4.7 (t, 1H, CH), 4.0-4.25 (m, 4H, CO_2CH_2), 3.30-3.50 (m, 6H, $CH_2CH_2CH_2$), 3.1-3.3 (m, 4H, NCH_2), 2.0-2.52 (m, 2H, CH_2), 1.6-1.95 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.1-1.48 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.28; H, 8.41. Found: C, 67.32; H, 8.44

Diethyl 8-(N-Pyrrolidinyl)-2,8-cyclooctadiene-1,2-dicarboxylate (3b).- Compound **2b** was refluxed in benzene for 5 h and the solvent was removed under reduced pressure. Column chromatography of the oily residue [silica gel, ethyl acetate- toluene (1:1)] afforded the pure product. MS (70 ev): 321 (M^+); IR (KBr): 1730 and 1660 (ester C=O), 1600 (C=C) cm^{-1} ; ^1H NMR: δ 6.7-6.95 (d-d, 1H, CH=C), 3.9-4.35 (m, 4H, CO_2CH_2), 3.1-3.5 (m, 4H, NCH_2), 2.05-2.45 (m, 8H, $CH_2CH_2CH_2CH_2$), 1.8-2.0 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.0-1.4 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.28; H, 8.41. Found: C, 67.40; H, 8.35

Diethyl 1-(N-Piperidinyl) bicyclo[4.2.0]octene-7,8-dicarboxylate (2c).- This compound could be isolated when **1c** was allowed to react similarly with DEAD in benzene solution. The solid was recrystallized from diethyl ether. MS (70 ev): 335 (M^+); IR (KBr):1680-1720 (ester C=O), 1580

(C=C)cm^{-1}; ^1H NMR: δ 4.4-4.7 (t, 1H, CH), 4.0-4.3 (m, 4H, CO_2CH_2), 3.7-3.8 (m, 4H, NCH_2), 2.6-3.2 (m, 6H, $CH_2CH_2CH_2$), 1.7-2.1 (m, 2H, CH_2), 1.5-1.7 (m, 6H, $NCH_2\mathbf{CH_2CH_2CH_2}$), 1.05-1.45 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{19}H_{29}NO_4$: C, 68.05; H, 8.65. Found: C, 67.91; H, 8.71

Diethyl 8-(N-Piperidinyl)-2,8-cyclooctadiene-1,2-dicarboxylate (3c).- Compound **2c** was refluxed in benzene for 5 h. The solvent was evaporated and column chromatography of the residue [silica gel, benzene - ethyl acetate (4:1)] afforded pure 3c. MS (70 ev): 335 (M^+); IR (KBr): 1720 and 1680 (ester C=O), 1620 (C=C) cm^{-1} ; ^1H NMR: δ 6.4-6.75 (d-d, 1H, CH=C), 3.9-4.37 (m, 4H, CO_2CH_2), 3.3-3.5 (m, 4H, NCH_2), 2.0-3.2 (m, 8H, $CH_2CH_2CH_2CH_2$), 1.4-1.8 (m, 6H, $NCH_2\mathbf{CH_2CH_2CH_2}$), 0.9-1.3 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{19}H_{29}NO_4$: C, 68.05; H, 8.65. Found: C, 68.18; H, 8.59

Compound 4.- A similar reaction between **1c** and DEAD in methanol gave **4** as an oil which could not be solidified. MS (70 ev): 335 (M^+); IR (KBr): 1730 and 1690 (ester C=O), 1580 (C=C) cm^{-1}; ^1H NMR: δ 5.0-5.3 (d-d, 1H, NCH), 4.0-4.1 (m, 4H, CO_2CH_2), 3.6-3.8 (m, 4H, NCH_2 and $NCH\mathbf{CH_2}$), 3.1-3.5 (d-d, 2H, $\mathbf{CH_2}CO_2CH_2CH_3$), 2.0-3.1 (m, 8H, $CH_2CH_2CH_2CH_2$), 2.0-3.1 (m, 4H, $NCH_2\mathbf{CH_2CH_2CH_2}$), 1.0-2.0 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{19}H_{29}NO_4$: C, 68.05; H, 8.65. Found: C, 67.77; H, 8.58

The general procedure for the reaction of enamines (**1a-c**) with DEAD was applied to **1d-f**, but we did not try to isolate [2+2] cycloadducts, **2d-f.** The reaction mixture was refluxed in benzene for 4 h and the cycloisomerization products, **3d-f**, were isolated.

Diethyl 7-(N-Morpholinyl)-2,7-cycloheptadiene-1,2-dicarboxylate (3d).- The oil was purified by column chromatography [silica gel, benzene - ethyl acetate (4:1)]. MS (70 ev): 323 (M^+); IR (KBr): 1740 and 1680 (esterC=O), 1580 (C=C) cm^{-1}; ^1H NMR: δ 6.5-6.7 (d-d, 1H, CH), 4.0-4.2 (m, 4H, CO_2CH_2), 3.6-3.8 (m, 4H, NCH_2), 2.9-3.1 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.6-2.75 (m, 6H, $CH_2CH_2CH_2$), 1.1-1.3 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{17}H_{25}NO_5$: C, 63.15; H, 7.73. Found: C, 63.31; H, 7.84

Diethyl 7-(N-Pyrrolidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate (3e).- The oil was purified by column chromatography [silica gel, toluene-ethyl acetate (1:1)]. MS (70 ev): 307 (M^+); IR (KBr): 1720 and 1680 (ester C=O), 1610 (C=C)cm^{-1} ; ^1H NMR: δ 6.6-6.75 (d-d,1H, CH), 4.3-4.5 (m, 4H, CO_2CH_2), 3.9-4.25 (m, 4H, NCH_2), 3.2-3.75 (m, 6H, $CH_2CH_2CH_2$), 1.80-2.0 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.1-1.45 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.44; H, 8.14. Found: C, 66.56; H, 8.08

Diethyl 7-(N-Piperidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate (3f).- The oil was purified by column chromatography [silica gel, toluene-ethyl acetate (1:1)]. MS (70 ev): 321(M^+); IR (KBr): 1720 and 1680 (ester C=O), 1580 (C=C) cm^{-1}; ^1H NMR: δ 6.7-7.0 (d-d, 1H, CH), 3.8-4.3 (m, 4H, CO_2CH_2), 3.1-3.4 (m, 4H, NCH_2), 1.9-2.6 (m, 6H, $CH_2CH_2CH_2$), 1.3-1.9 (m, 6H, $NCH_2\mathbf{CH_2CH_2CH_2}$), 0.9-1.25 (m, 6H, $CO_2CH_2\mathbf{CH_3}$).

Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.28; H, 8.41. Found: C, 67.39; H, 8.20

General Procedure for the Reaction of Enamines (5a-c) with DMAD.- Ninety mmol enamine (**5a-c**) in 15 mL benzene was added dropwise to a solution of 40 mmol (4.16 mL) DMAD in 10 mL benzene. The reaction mixture was stirred for 3 days at room temperature. Then, an additional 50 mmol (7.96 mL) DMAD was introduced and the mixture was stirred for another 4 days. The solvent was removed and purification by column chromatography afforded pure **6a-c**.

Dimethyl 2a,3,4,8b-Tetrahydro-8b-(N-morpholinyl)-cyclobuta[a]napthalene-1,2-dicarboxylate (6a).- This compound could be crystallized after column chromatography. MS (70 ev): 357 (M^+);IR (KBr): 1710 and 1690 (ester C=O), 1640 (C=C), 1600-1400 (aromatic CH) cm^{-1}; ^1H NMR: δ 8.0-8.10 (m, 1H, ArH), 6.9-7.4 (m, 3H, ArH), 3.8-3.95 (s,6H, CO_2CH_3), 3.65-3.79 (t, 1H, HC-C=), 3.5-3.60 (m, 4H, NCH_2), 2.3-2.9 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.4-2.0 (m, 4H, CH_2CH_2).

Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.22; H, 6.44. Found: C, 67.16; H, 6.31

Dimethyl 2a,3,4,8b-Tetrahydro-8b-(N-pyrrolidinyl)-cyclobuta[a]napthlene-1,2-dicarboxylate (6b).- MS (70 ev): 341(M^+); IR (KBr): 1720 and 1680 (ester C=O), 1620 (C=C), 1600-1400 (aromatic CH) cm^{-1}; ^1H NMR: δ 7.8-8.10 (m, 1H, ArH), 6.9-7.5 (m, 3H, ArH), 3.8-3.90 (s, 3H, CO_2CH_3), 3.75-3.85 (t,1H, HC=C), 3.5-3.7 (m, 4H, NCH_2), 2.5-2.80 (m, 4H, NCH_2 $\mathbf{CH_2}$), 1.35-2.4 (m, 4H, CH_2CH_2).

Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.38; H, 6.74. Found: C, 70.20; H, 7.02

Dimethyl 2a,3,4,8b-Tetrahydro-8b-(N-piperidinyl)cyclobuta[a]napthalene-1,2-dicarboxylate (6c).- MS (70 ev): 355 (M^+); IR (KBr): 1740 and 1680 (ester C=O), 1620 (C=C), 1600-1400 (aromatic CH)cm^{-1}; ^1H NMR: δ 8.0-8.2 (m, 1H, ArH), 6.95-7.45 (m, 3H, ArH), 3.8 (s, 6H, CO_2CH_3), 3.4-3.6 (t, 1H, HC-C=), 3.0-3.25 (m, 4H, NCH_2), 1.4-2.9 (m, 4H, CH_2CH_2), 1.1-1.3 (m, 6H, $NCH_2\mathbf{CH_2CH_2}CH_2$).

Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.98; H, 7.04. Found: C, 70.83; H, 7.12

General Procedure for the Reaction of Enamines (7a-c) with DMAD.- A solution of 14 mmol **7a-c** and 14 mmol (1.72 mL) DMAD in benzene was refluxed for 4-5 h. The solvent was removed and column chromatography [silica gel, ethyl acetate-toluene (4:1)] of the crude product gave pure **8a-c** as oil.

Dimethyl 1-(N-Morpholinyl)-4-ethyl-1-cyclobutene-1,2-dicarboxylate (8a).- MS (70 ev): 283 (M^+); IR (KBr): 1745 and 1560 (ester C=O), 1440 (C=C) cm^{-1}; ^1H NMR: δ 5.90 (m, 1H, CH), 4.85 (d, 1H, CH), 3.9-4.2 (m, 4H, NCH_2), 3.75 (s, 6H, CO_2CH_3), 3.3 (m, 4H, NCH_2 $\mathbf{CH_2}$), 2.3 (m, 2H, CH_2), 0.9-1.4 (m, 3H, CH_3).

Anal. Calcd for $C_{14}H_{21}NO_5$: C, 59.36; H, 7.42. Found: C, 59.10; H, 7.67

Dimethyl 1-(N-Pyrrolidinyl)-4-ethyl-1-cyclobutene-1,2-dicarboxylate (8b).- MS (70 ev): 267 (M^+); IR (KBr): 1750 and 1660 (ester C=O), 1560 (C=C) cm^{-1}; ^1H NMR: δ 5.75 (m, 1H, CH), 4.5 (d, 1H, CH), 3.85 (s, 6H, CO_2CH_3), 3.0-3.4 (m, 4H, NCH_2), 2.2-2.4 (m, 4H, $NCH_2\mathbf{CH_2}$), 1.7-2.1 (m, 2H, CH_2), 1.0-1.3 (m, 3H, CH_3).

Anal. Calcd for $C_{14}H_{21}NO_4$: C, 62.92; H, 7.86. Found: C, 62.72; H, 7.66

Dimethyl 1-(N-Piperidinyl)-4-ethyl-1-cyclobutene-1,2-dicarboxylate (8c).- MS (70 ev): 281 (M^+); IR (KBr): 1745 and 1680 (ester C=O), 1460 (C=C) cm^{-1}; ^1H NMR: δ 5.85 (m, 1H, CH), 4.75 (d, 1H,

CH), 3.75 (s, 6H, CO_2CH_3), 3.0-3.3 (m, 4H, NCH_2), 2.4-2.6 (m, 2H, CH_2), 1.4-1.6 (d-d, 6H, $NCH_2\mathbf{CH_2CH_2CH_2}$), 0.9-1.1 (m, 3H, CH_3).

Anal. Calcd for $C_{15}H_{23}NO_4$: C, 64.05; H, 8.18. Found: C, 63.78; H, 8.09

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