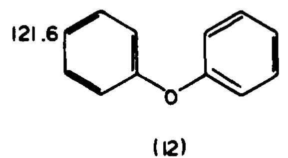
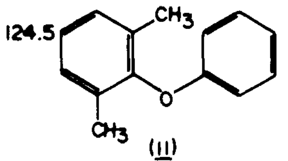
J. Org. Chem. 1982, 47, 4353–4356



(12)



(11)

The above observation has led us to propose that analogous conformational changes occur with respect to rings C and C′ of **2** (1*S*,1′*R*) and **5** (1*S*,1′*S*).

Dreiding model analysis of **2** and **5** reveals that the A and A′ diphenyl ether moieties also suffer conformational changes in these two diastereomeric compounds. The fact that C-5 and C-4a′ (para to ether linkages) resonate at lower fields in **5** than in **2** indicates the occurrence of wider interplanar angles between A and A′ in the repandine series.

The lack of ^{13}C NMR data for obaberine (**13**), which would be comparable to *O*-methylrepandine (**6**), was compensated for by ^{1}H NMR spectroscopic observations. The 6′- and 7-methoxy groups of **13** resonate at δ 3.63 and 3.20, while those of **6** resonate at δ 3.42 and 3.03, respectively.[5] Molecular models of these two diastereomeric compounds, together with ^{1}H NMR spectroscopy observations, reveal that the planes of rings A and A′ are tilted at an angle of about 70° to one another in **13**. As a result, the protons of the 7-methoxyl groups are brought above the shielding zone of ring A′, but the 6′-methoxy group remains outside the shielding zone of A. On the other hand, in compound **6** the larger interplanar angle between A and A′ brings both the 7- and 6′-methoxyl groups above the aromatic shielding zones.

The chemical shifts of the H-8′ protons further confirm the angular modifications in both AA′ and CC′ ether linkages which occur in the 1*S*,1′*R* and 1*S*,1′*S* series. In obaberine (**13**), H-8′ appears at an abnormally high field (δ 5.48)[5] as a consequence of the anisotropic shielding of rings C and C′, while H-8′ of **6** lies in the shielding zone of ring C and deshielding zone, of C′; these two effects evidently cancel each other out, and the proton resonates further downfield (δ 6.38).

From the foregoing considerations, it is suggested that none of the benzylisoquinoline moieties in this series acquires a fully folded conformation in solution. This results in less flexible molecules, and the difference in absolute configuration at C-1′ for the repandine series causes an increase in the interplanar angles between rings AA′ and CC′ as compared to those for the daphnoline series. It would appear from this and previous conformational studies[2] that in order to acquire a folded conformation, the coclaurine units of a bis(benzylisoquinoline) must be unsubstituted at C-8, and their benzyl groups should have a para diphenyl ether link. These conditions do not occur in the daphnoline–repandine series, so that the extended conformation prevails.

Experimental Section

The ^{13}C NMR spectra were obtained in a 10-mm spinning tube from solutions of approximately 0.5 mmol of compound in 1 mL of solvent. The instrument employed was Varian XL-100 NMR spectrometer operating at 25.2 MHz and interfaced with a Varian 620-L Fourier transform computer with a 16K memory. The chemical shifts (±0.05 ppm) were measured at a 5-kHz spectral width, with an acquisition time of 0.8 s and a 15-μs pulse width, by using an internal deuterium lock.

Registry No. 1, 479-36-7; **2**, 519-53-9; **3**, 1183-76-2; **4**, 24306-66-9; **5**, 518-92-3; **6**, 4021-17-4.

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(6) Buchanan, G. W.; Montaudo, G.; Finocchiaro, P. *Can. J. Chem.* **1974**, *52*, 767.

Conformational Analysis. 43. A Boat-Shaped Piperidine Ring in 3-Thia-7-aza-6,8-diphenylbicylco[3.3.1]nonan-9-ol[1]

Ernest L. Eliel,* Muthiah Manoharan, Derek J. Hodgson,* and Drake S. Eggleston

W. R. Kenan, Jr., Laboratories, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

R. Jeyaraman

Department of Chemistry, American College, Madurai 625002, Tamil Nadu, India

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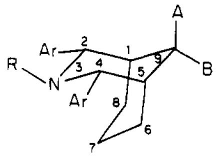
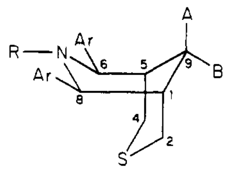
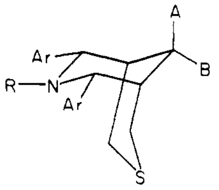
On the basis of an extensive tabulation[2] of the ^{13}C NMR spectra of a series of 2,4-diarylazabicyclo[3.3.1]nonanes and the corresponding 9-ones and 9-ols (two epimers; **1**) it was concluded, in accordance with other evidence[3] that these compounds exist largely or entirely in double-chair conformations. An exception was found, however, in the corresponding 7-thia compounds **2** (properly named 3-thia-7-aza-6,8-diarylbicyclo[3.3.1]nonanes). The salient ^{13}C NMR data[2] for the nonaromatic carbons are reproduced in Table I.



1



2



3

A = B = H; A = OH, B = H
A = H, B = OH, A, B = =O; R = H or Me

In comparing the 9-keto compounds (**1a,b** vs. **2a,b**; see Table I for definitions of **a–d**) one notes a palpable upfield shift of the benzylic carbons C(2,4) (numbering for **1**; ca. 1.3 ppm) in going from the carbons compounds (**1a**, **1b**) to the thia compounds (**2a**, **2b**) and an even larger upfield shift (4 ppm or more) for C(9), the carbonyl carbon. The shifts for C(9) and also for C(1,5) and C(6,8) should properly be compared to similar shifts as one goes from cyclohexanone to 4-thiacyclohexanone; the comparison is as follows (cyclohexanone − thiacyclohexanone differences in parentheses):[4] C(6,8), 8.3–8.4 (2.9); C(1,5), 1.0–1.2 (2.1); C(9), −4.0 to −4.4 (−3.3). It is especially the large discrepancy at C(6,8) [C(2,4) in the thia system] that suggests that compounds **2a** and **2b** are not chair–chair conformations.

This hypothesis is corroborated by the chemical shifts in the alcohols **2c** and **2d**. When an axial hydroxyl group

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(1) Paper 42. Eliel, E. L.; Hargrave, K. D.; Pietrusiewicz, K. M.; Manoharan, M. *J. Am. Chem. Soc.* **1982**, *104*, 3635.

(2) Jeyaraman, R.; Jawaharsingh, C. B.; Avila, S.; Ganapathy, K.; Eliel, E. L.; Manoharan, M.; Morris-Natschke, S., *J. Heterocycl. Chem.*, **1982**, *19*, 449.

(3) Jeyaraman, R.; Avila, S. *Chem. Rev.* **1981**, *81*, 149.

(4) Hirsch, J. A.; Havinga, E. *J. Org. Chem.* **1976**, *41*, 455.

0022-3263/82/1947-4353$01.25/0

Table I. ^{13}C NMR Data for 1 and 2

structure	C(1,5)	C(2,4)[a]	C(6,8)[b]	C(7)	C(9)	NMe
1a, Ar = C_6H_5, R = H, A = B = =O	54.0_5	64.8_4	29.0_8	21.2_0	217.2_0	
1b, Ar = *p*-ClC_6H_4, R = H, A = B = =O	53.7_8	64.2_1	28.9_4	21.1_7	215.9_6	
1c, Ar = C_6H_5, R = H, A = OH, B = H	42.1_3	57.8_6	26.3_0	21.1_8	74.1_2	
1c′, Ar = C_6H_5, R = H, A = H, B = OH	41.6_4	64.0_2	19.3_7	20.9_9	74.5_5	
1d, Ar = C_6H_5, R = Me, A = OH, B = H	43.5_3	66.8_2	26.6_6	20.6_2	73.3_8	44.0_1
1d′, Ar = C_6H_5, R = Me, A = H, B = OH	42.9_5	73.6_5	19.6_9	20.5_7	74.5_2	44.1_5
2a, Ar = C_6H_5, R = H, A = B = =O	55.0_6	63.5_8[a]	37.4_4[b]		212.7_8	
2b, Ar = *p*-ClC_6H_4, R = H, A = B = =O	54.9_4	62.8_8[a]	37.3_4[b]		211.9_6	
2c, Ar = C_6H_5, R = H, A = OH, B = H	42.3_8	62.1_4[a]	34.1_7[b]		73.7_1	
2d, Ar = C_6H_5, R = Me, A = OH, B = H	44.6_3	71.1_7[a]	33.5_3[b]		72.5_5	47.0

[a] C(6,8) in **2**. [b] C(2,4) in **2**.

Table II. Positional Parameters for 2c

atom	*x*	*y*	*z*
S	−1	0	−1
O	−0.5000 (5)	0	−0.2558 (6)
N	−0.4315 (5)	0	−0.6912 (7)
C1	−0.7017 (4)	−0.0606 (2)	−0.6166 (6)
C2	−0.9180 (5)	−0.0673 (2)	−0.7887 (8)
C8	−0.5547 (4)	−0.0597 (2)	−0.7581 (5)
C9	−0.6807 (6)	0	−0.4606 (8)
CP1	−0.4163 (4)	−0.1180 (2)	−0.7059 (6)
CP2	−0.2885 (5)	−0.1310 (2)	−0.4693 (6)
CP3	−0.1583 (6)	−0.1834 (2)	−0.4257 (8)
CP4	−0.1555 (6)	−0.2229 (2)	−0.6129 (8)
CP5	−0.2810 (6)	−0.2102 (2)	−0.8478 (8)
CP6	−0.4109 (5)	−0.1581 (2)	−0.8920 (7)
H1C1	−0.684 (5)	−0.100 (2)	−0.514 (5)
H1C2	−0.940 (5)	−0.103 (2)	−0.908 (6)
H2C2	−0.997 (6)	−0.078 (2)	−0.699 (8)
H1C8	−0.619 (4)	−0.059 (1)	−0.934 (5)
H1C9	−0.801 (8)	0	−0.389 (9)
HCP2	−0.290 (5)	−0.105 (2)	−0.351 (6)
HCP3	−0.066 (7)	−0.190 (2)	−0.242 (8)
HCP4	−0.062 (8)	−0.257 (3)	−0.574 (9)
HCP5	−0.293 (5)	−0.236 (2)	−0.974 (6)
HCP6	−0.482 (5)	−0.150 (2)	−1.055 (5)
HN	−0.300	0	−0.620
HO	−0.390	0	−0.320

is introduced in a cyclohexane chair, a sizable (ca. 6 ppm) upfield shift of the γ-carbon atom (γ_{gauche} shift) results. This shift is seen at C(2,4) in **1c** and **1d** (as compared to the corresponding shifts in the ketone **1a** or the epimers **1c′** and **1d′**, and at C(6,8) in **1c′** and **1d′** (again compared to the ketone **1a** or the epimers **1c** and **1d**). In contrast, the upfield shift at C(6,8) in going from ketone **2a** to alcohol **2c** is very small (1.4 ppm) and that at C(2,4), 3.2 ppm, compares closely to the shift of 2.8 ppm, which one sees in going from ketone **1a** [C(6,8)] to alcohol **1c** in which the hydroxyl group is equatorial to the carbocyclic ring. We also note the 3-ppm downfield shift of the NMe signal as between **2d** and **1d**.

While it seems quite clear from the preceding argument that the thia compounds **2** are not in chair–chair conformations, a question remains, as to whether it is the nitrogen-containing ring (**2**) or the sulfur-containing one (**3**), which is in the boat form. Because of the absence of a γ_{gauche} effect in the thia alcohols, if conformation **2** pertains, A = OH, but if conformation **3** is correct, B = OH; thus the configuration of the alcohol function at C(9) is uncertain also. In our previous paper[2] we argued that if conformation **3** were the correct one for the 9-one, the transannular (OH/S) compression in the 9-ol might throw this compound partially or entirely back to the chair form, especially since boat conformations are more unstable in saturated cyclohexanes than in cyclohexanones.[5,6] Since no such conformational change is evident, we opted for conformation **2**. This has now been confirmed by X-ray structure analysis of compound **2c**.

Experimental Section

An opaque, colorless crystal of **2c**[2] was found to be monoclinic, space group *Cm*, *a* = 7.222 (2), *b* = 20.544 (17), *c* = 5.829 (5) Å, β = 110.41 (6)°, volume = 810.46 Å^3, *Z* = 2, D_{calcd} = 1.28, D_{meas} = 1.25 (2) g cm^{-3} (flotation in aqueous potassium iodide). Cell constants were obtained on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation and a graphite monochromator. Intensity data were collected in a θ–ω scan mode out to 2θ(Mo) = 60°. The data were corrected for Lorentz–polarization effects but not for absorption (μ = 2.01 cm^{-1} for these atoms). Excluding 98 "unobserved" data, 1120 unique reflections with $I \geq 3\sigma(I)$ were used in the subsequent analysis. No systematic absences, other than those required by the C-centering, were observed. Thus, the possible space groups are *C*2/*m*, *Cm*, and *C*2, but with *Z* = 2 the only ordered possibility for this molecule is *Cm*.

In space group *Cm* the origin is undefined and the molecule is required to sit on a crystallographic mirror plane. Necessarily, this plane must pass through the sulfur, nitrogen, and oxygen atoms as well as the carbon atom bonded to the hydroxyl group. Therefore, the coordinates of the heaviest atom, sulfur, were fixed as the origin. A subsequent difference Fourier map was sufficiently well-phased to yield positions for all heavy atoms. Isotropic least-squares refinement of all 13 unique heavy atom positions led to values of the agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.158 and 0.157, respectively, where the weights *w* were assigned as $4F_o^2/\sigma^2(F_o^2)$. Following the inclusion of anisotropic librational parameters for the non-hydrogen atoms, three cycles of least-squares refinement yielded R_1 = 0.097 and R_2 = 0.109, and a difference Fourier map

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(5) Cf. Zefirov, N. S. *Russ. Chem. Rev. (Engl. Transl.)* **1975**, *44*, 196, for a detailed discussion of this point.

(6) In detailed studies involving a combination of electron diffraction and molecular mechanics, Mastryukov, V. S.; Popik, M. V.; Dorofeeva, O. V.; Golubinskii, A. V.; Vilkov, L. V.; Belikova, N. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 1333, found less than 5% of the boat conformation in bicyclo[3.3.1]nonane at 65 °C. In contrast, Raber, D. J.; Janks, C. M.; Johnston, M. D., Jr.; Raber, N. K. *Tetrahedron Lett.* **1980**, *21*, 677, found 22% boat form in bicyclo[3.3.1]nonan-9-one at room temperature by LIS experiments.

Table III. Intramolecular Distances (Å) and Angles (deg) in **2c**

distances			
S–C2	1.809 (2)	C1–C2	1.540 (2)
C1–C8	1.555 (2)	C1–C9	1.518 (2)
C8–N	1.486 (2)	C8–CP1	1.521 (2)
C9–O	1.429 (3)	CP1–CP2	1.392 (2)
CP2–CP3	1.394 (2)	CP3–CP4	1.366 (3)
CP4–CP5	1.378 (3)	CP5–CP6	1.388 (3)
CP6–CP1	1.393 (3)		
bond angles			
C2–S–C4	99.7 (2)	C2–C1–C8	112.4 (2)
C2–C1–C9	109.3 (2)	C8–C1–C9	111.3 (1)
S–C2–C1	113.1 (1)	C1–C8–N	109.1 (1)
C1–C8–CP1	114.0 (1)	N–C8–CP1	107.8 (1)
C6–N–C8	111.4 (2)	C1–C9–C5	110.3 (2)
C1–C9–O	111.8 (1)	C8–CP1–CP2	120.8 (1)
C8–CP1–CP6	120.8 (1)	CP2–CP1–CP6	118.4 (1)
CP1–CP2–CP3	120.1 (2)	CP2–CP3–CP4	120.7 (2)
CP3–CP4–CP5	119.6 (2)	CP4–CP5–CP6	119.9 (2)
CP5–CP6–CP1	121.3 (2)	C9–O–HO	124 (2)
C8–N–HN	121 (2)		
torsion angles			
C9–C1–C2–S	−61.7	C9–C1–C8–N	−2.4
C5–C9–C1–C2	70.4	C5–C9–C1–C8	−54.0
C1–C8–N–C6	60.8	O–C9–C1–C8	71.1
C1–C2–S–C4	48.8	O–C9–C1–C2	−164.5

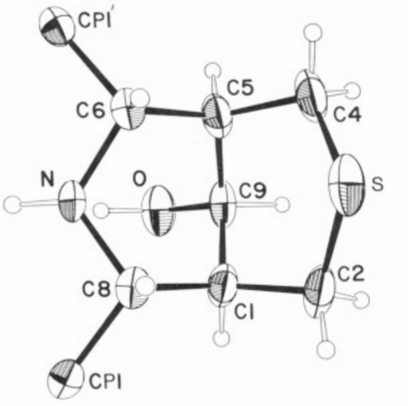


Figure 1. View of the 3-thia-7-aza-6,8-diphenylbicyclo[3.3.1]-nonan-8-ol molecule. Only the ipso carbon atoms CP1 and CP1′ of the phenyl rings are shown. Note that the atom pairs (C8, C6), (C1, C5), (C2, C4) are related by the crystallographic mirror plane that passes through N, S, O, C9.

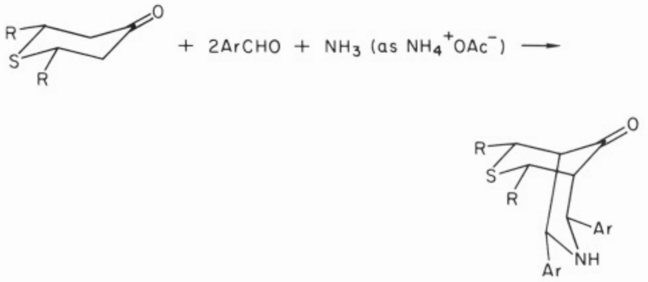
revealed positions for all hydrogen atoms except the one bonded to nitrogen. The position of the amino hydrogen atom was calculated from theoretical considerations (NH = 0.90 Å) and, along with the hydroxyl proton position, was fixed in all subsequent least-squares refinements. Isotropic thermal parameters were included for all hydrogen atoms. A correction for secondary extinction was also included in the last stages of refinement. The final cycle of least-squares refinement (1120 observations, 144 variables) converged to values of 0.059 and 0.066 for R_1 and R_2, respectively. The atomic positional parameters derived from the final least-squares cycle are listed in Table II.

Table III shows the principal bond lengths, bond angles, and torsional angles found for **2c**. Tables of bond lengths involving hydrogen atoms, amplitudes of libration, and observed and calculated structure amplitudes are available as supplementary material.

Discussion

As can been seen from Figure 1, the conformation of the sulfur-containing ring (S–C2–C1–C9–C5–C4) is indeed a chair, while that of the nitrogen-containing ring (N–C8–C1–C9–C5–C6) is a boat. The conformations may be described by the deviations of the apical atoms from the four-atom least-squares planes for each ring. Thus sulfur sits 0.812 Å above and C9 0.775 (4) Å below the C2–C4–C1–C5 plane, while nitrogen and C9 both sit below the C8–C6–C1–C5 plane by 0.692 (4) and 0.657 (4) Å, respectively. The dihedral angle between the plane defined by the phenyl ring and the C8–C6–C1–C5 plane is 105.3°. The hydroxyl group is disposed equatorially to the sulfur-containing ring, but there is no evidence for either intramolecular or intermolecular hydrogen bonding. All bond lengths and angles are within the ranges expected for this type of structure. The unusually large C5–C9–C1–C2 and the small C1–C2–S–C4 torsion angles suggest that the "flaps" of the sulfur-containing chair tend to move away from C6–N–C8 and the substituents at C6, C8 of the nitrogen-containing boat. The agreement of the crystallographic findings with the deductions made from the ^{13}C NMR spectra (vide supra) suggest agreement of the predominant conformation in solution with that found in the crystal.

Scheme I



Chair–boat conformations in hetera[3.3.1]bicyclononanes have been observed before;[5] for example, Zefirov[7] et al. have found 3,7-dithia-9-oxa[3.3.1]bicyclononane to be in the chair–boat form, though the 3,9-dithia-7-oxa analogue is a double chair.[7] The result has been explained[5,7] in terms of lone-pair/lone-pair repulsions. After this work was completed, a paper appeared by Pantaleo, van der Helm, Berlin, and co-workers, describing a chair–boat structure in 2,4,6,8-tetraphenyl-3-thia-7-azabicyclo[3.3.1]nonan-9-one.[8,9] Our case is similar to that described by these investigators, but there is one significant difference. The tetraphenyl compounds are synthesized by condensing *cis*-2,6-diphenyl-1-thiacyclohexan-4-ones with benzaldehyde and ammonia (Scheme I, R = Ar). Since the two phenyl groups hold the thiacyclohexanone starting material rigidly in the chair form, the alternatives are for the condensation to produce a chair–chair conformation or a chair–boat conformation in which the nitrogen-containing ring is the boat. (Both products would be conformationally rigid.) Evidently the steric interference in the double-chair product is so large that the corresponding transition state in the condensation is disfavored and the (more stable) chair–boat structure results.

In our case (Scheme I, R = H) there are more degrees of freedom. It might be possible for the condensation to proceed toward the double chair with steric compression being relieved either after, or more likely during, the reaction by an inversion of the sulfur-containing ring to a boat form. This would lead to a chair–boat of type **3**

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[7] Zefirov, N. S.; Rogozina, S. V.; Kurkutova, E. N.; Goncharov, A. V.; Belov, N. V. *Chem. Commun.* **1974**, 260. Zefirov, N. S.; Kurkutova, E. N.; Goncharov, A. V. *J. Org. Chem. USSR* **1974**, *10*, 1137.

[8] Pantaleo, N. S.; van der Helm. D.; Ramarajan, K.; Bailey, B. R.; Berlin, K. D. *J. Org. Chem.* **1981**, *46*, 4199.

[9] The occurrence of (rigid) chair–boat conformations in 2,4,6,8-tetraarylazabicyclononanes is perhaps not exceptional. We have (by ^{13}C NMR) found the chair–boat conformation in 2,4,6,8-tetraaryldiazabicyclononanes in which the aryl groups are *p*-anisyl or *p*-chlorophenyl: Eliel, E. L.; Manoharan, M.; Jeyaraman, R., unpublished observations.

(above). One might even imagine this structure to be formed by a prior inversion of the thiacyclohexanone starting material to a boat form. Attractive as this possibility might appear, it is not the path the molecule chooses. Rather it reacts in the same manner as the tetraphenyl compound studied by the Oklahoma group.[8] The thiacyclohexanone remains in the chair form; the steric compression in the chair–chair product is avoided by forming the nitrogen-containing ring as a boat; the product (except for the unlikely change to a double boat) is conformationally rigid.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE80-20388) for financial support.

Registry No. 2c (Ar = C_6H_5; R = B = H; A = OH), 82918-33-0.

Supplementary Material Available: Tables S1 (bond lengths involving hydrogen atoms) and S2 (anisotropic thermal parameters) (2 pages). Ordering information is given on any current masthead page.

A Novel Photochemical [3 + 2] Cycloaddition of 3-Cyano-5,5-dimethyl-2-cyclohexenone to Olefins[1]

Isao Saito,* Koji Shimozono, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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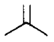
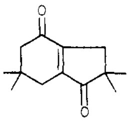
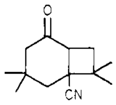
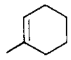
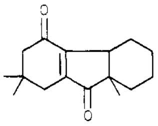
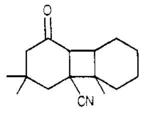
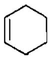
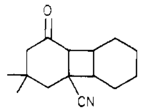
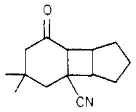
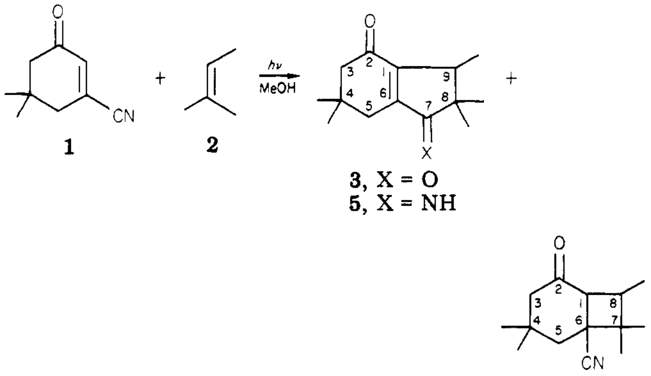
The inter- and intramolecular [2 + 2] photocycloaddition of cyclic enones to olefins has been the subject of synthetic and mechanistic investigations.[2] The intermediacy of enone triplet and subsequent 1,4-biradical formation are well-documented in many cases.[2,3] We have recently noted that cyano-substituted heterocycles such as 6-cyanouracils[4] and 2-cyanopyridine[5] undergo anomalous addition with olefins resulting in 1,4-transfer of cyano group or the formation of [3 + 2] adduct by interception of the intermediate biradicals by the cyano groups.[6] In further extending this study, we describe here a new temperature-dependent [3 + 2] photochemical cycloaddition of 3-cyanocylohexenone to olefins that competes with normal [2 + 2] cycloaddition.[7]

3-Cyano-5,5-dimethyl-2-cyclohexenone (**1**, 30 mM) was irradiated in methanol with a high-pressure mercury lamp (Pyrex filter) in the presence of 2-methyl-2-butene (**2**, 0.3 M) for 5 h at room temperature. Removal of the solvent followed by preparative TLC (silica gel, hexane–ethyl acetate) afforded two photoproducts **3** (35%) and **4** (30%). The assigned structures are based on their spectral data. Support for the enedione structure of **3** is furnished by the low-field ^{13}C NMR signals (149.0, 159.9, 199.3, and 214.8 ppm), two carbonyl stretching bands (1710 and 1680 cm^{-1}) in the IR, and a UV absorption at 258 nm. The ^1H NMR showed a long-range coupling (J = 2.5 Hz) attributable to homoallylic coupling between the C-5 methylene group and the C-9 methine proton, indicating the orientation of the adduct **3**. The enedione **3** was formed from bicyclic imine **5** during workup. In fact, **5** was isolated by careful preparative high-performance liquid chromatography. Treatment of hydrolytically sensitive **5** with a catalyic amount of HCl immediately produced **3**. The orientation of the [2 + 2] cycloadduct **4** is apparent from the vicinal coupling (J = 10.5 Hz) between the C-1 and C-8 methine protons in the ^1H NMR spectrum. However, we were not confident in assigning the stereochemistry of **4**, although no change in the ^1H NMR resulted upon treatment of **4** with basic alumina, suggestive of the cis ring junction of **4**.[8]

Table I. Photoaddition of 3-Cyano-5,5-dimethyl-2-cyclohexenone (1) to Olefins[a]

no.	olefin	product (%)[b]	
1[c]		 **6** (38)	 **7** (46)
2		 **8** (35)	 **9** (30)
3		ND[d]	 **10** (80)
4		ND[d]	 **11** (75)

[a] Solutions of **1** (20 mM) and olefins (50 mM) in methanol were irradiated with a 100-W high-pressure mercury lamp (Pyrex filter) at room temperature under the standard conditions described in the Experimental Section. [b] Yields are for isolated pure products. [c] See the Experimental Section for reaction conditions. [d] Not detected.



1 **2** **3**, X = O
5, X = NH

4

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(1) Photoinduced Reactions. 140.

(2) (a) Eaton, P. E. *Acc. Chem. Res.* **1971**, *2*, 41. (b) Bauslaugh, P. G. *Synthesis* **1970**, 287. (c) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. (d) Dilling, W. L. *Photochem. Photobiol.* **1977**, *25*, 605.

(3) For a recent example, see: Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559 and references therein.

(4) (a) Saito, I.; Shimozono, K.; Matsuura, T. *J. Am. Chem. Soc.* **1980**, *102*, 3948. (b) Saito, I.; Shimozono, K.; Miyazaki, S.; Matsuura, T.; Fukuyama, T.; Katsube, Y. *Tetrahedron Lett.* **1980**, *21*, 2317.

(5) Saito, I.; Kanehira, K.; Shimozono, K.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 2737.

(6) Several recent examples for anomalous photoadditions involving rearrangement of 1,4-biradicals include the following: (a) Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378. (b) Wagner, P. J.; Lin, K-C; Noguchi, Y. *Ibid.* **1981**, *103*, 3837. (c) Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.

(7) Photoaddition of 3-cyano-2-cyclohexenones with olefins and *tert*-butyl alcohol has previously been reported. (a) Agosta, W. C.; Lawrance, W. W., Jr. *J. Org. Chem.* **1970**, *35*, 3851. (b) Cantrell, T. S. *Tetrahedron* **1971**, *27*, 1227. (c) Kuemmerle, E. W., Jr.; Rettig, T. A.; Still, J. K. *J. Org. Chem.* **1975**, *40*, 3665.

(8) Corey, E. J.; Le Mahieu, R.; Bass, J. D.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

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