

# Relative Stability of Cyclic Olefins. II.

## Calculations on 1-, 3-, and 4-Methyl-Substituted Cyclenes

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The relative stabilities of 1-, 3-, and 4-methyl-substituted cyclobutenes and cyclopentenes have been analyzed in terms of nonbonded interactions and  $\sigma$ -bond stabilization energies. It is shown that the latter effect accounts for the major part of the stabilization of the 1-methyl derivatives. The  $\sigma$ -bond stabilization energy in 1-methylcyclobutene is significantly larger than in the corresponding cyclopentene derivative which can be explained in terms of increased *s* character of the  $C_1$  orbital participating in the  $C_1-C_{exo}$  bond, resulting from strain in the four-membered ring. The result of calculations on the relative stability of 3- and 4-methylcyclopentenes, based on nonbonded interactions only, are compatible with the experimental data.

Of the various thermochemical data presented in part I<sup>1</sup> the relative stabilities of the 1-, 3-, and 4-methyl-substituted cyclenes seem to be most readily susceptible to theoretical analysis, since, unlike the *exo-endo* equilibria, they do not depend on the conformation of the ring, which should be very nearly identical in all three isomers.

$C=C$  1.34 Å., all  $C-H$  bonds 1.09 Å. and  $C_1=C_2-C_3$  93.7° (see Figure 1 for numbering of atoms). The HCH and  $HCC_{exo}$  angles which have not been determined experimentally are assumed by us to be 114° like the HCH angle in cyclobutane.<sup>5</sup> The exocyclic  $C_2=C_1-C_{exo}$  and  $C_2=C_1-H$  angles on the other hand were taken such as to equalize nonbonded  $C_{2,4}\cdots C_{exo}$ ,  $C_{2,4}\cdots H$  distances, respectively, in accordance with electron diffraction results on isobutylene.<sup>6</sup>

In the methylcyclopentene isomers the cyclic angles were derived on the assumption that the planar ring has  $C_{2v}$  symmetry and that all  $C-C-C$  angles are equal, which gives  $C=C-C \sim 111^\circ$  and  $C-C-C \sim 106^\circ$ , using bond lengths as in cyclobutene. The HCH and  $HCC_{exo}$  angles were assumed to be normal (109.5°).

Approximate calculations further showed that interactions with methyl group hydrogens are similar in both isomers and could therefore be neglected.

In order to estimate the effect of differences between nonbonded interaction potential functions we have chosen three vastly different sets of curves which all have been used before in calculations similar to those described here (see Table I).

Table I. Potential Functions Used (c.g.s. units)

Potential	Designation		Ref.
$V_{CC}$	A	$20.8 \times 10^{-10} r^{-12} - 22.6 \times 10^{-60} r^{-6}$	7
	B	$20.92 \times 10^{-10} [\exp(-3.42r \times 10^{+8})] - 29.29 \times 10^{-60} r^{-6}$	11
	C	$190 \times 10^{-10} [\exp(-4.782r \times 10^{+8})] - 9.95 \times 10^{-60} r^{-6}$	10
$V_{CH}$	A	$8.68 \times 10^{-60} \{ 358 [\exp(-r/0.490 \times 10^{-8})] - 1 \} r^{-6}$	7
	B	$20.92 \times 10^{-10} [\exp(-4.13r \times 10^{+8})] - 9.50 \times 10^{-60} r^{-6}$	11
	C	$15.1 \times 10^{-10} [\exp(-4.16r \times 10^{+8})] - 5.83 \times 10^{-60} r^{-6}$	8,9,10
$V_{HH}$	A	$4.58 \times 10^{-10} [\exp(-r/0.245 \times 10^{-8})] - 3.42 \times 10^{-60} r^{-6}$	7
	B	$20.92 \times 10^{-10} [\exp(-5.00r \times 10^{+8})] - 3.00 \times 10^{-60} r^{-6}$	11
	C	$1.20 \times 10^{-10} [\exp(-3.54r \times 10^{+8})] - 3.42 \times 10^{-60} r^{-6}$	8,9

*The Equilibrium between 1- and 3-Methyl-Substituted Cyclenes.* The factors affecting the equilibrium between 1- and 3-methyl-substituted cyclenes are (a) nonbonded interactions and (b) the "hyperconjugation" or  $\sigma$ -bond stabilization energy.<sup>2</sup>

(a) Dimensions of the methylcyclobutenes for the calculation of nonbonded interactions were taken from the electron diffraction analysis of 1-methylcyclobutene by Shand, Schomaker, and Fischer,<sup>3</sup> which agree with more recent data on cyclobutene.<sup>4</sup> Bond lengths and angles in this molecule, the ring carbons of which are coplanar, are as follows: all  $C-C$  bonds 1.54 Å.,

(1) J. Herling, J. Shabtai, and J. Gil-Av, *J. Am. Chem. Soc.*, **87**, 4107 (1965).

(2) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(3) W. Shand, V. Schomaker, and J. R. Fischer, *J. Am. Chem. Soc.*, **66**, 636 (1944).

(4) E. Goldish, K. Hedberg, and V. Schomaker, *ibid.*, **78**, 2714 (1956).

The potentials given by Bartell<sup>7</sup> are generally the hardest, while the theoretical De Boer<sup>8,9</sup>-Hirschfelder<sup>10</sup> curves predict much smaller interaction energies. Kitaigorodskii's<sup>11</sup> curves are somewhere in between, but they produce relatively larger  $C-C$  repulsions in the range of distances occurring in the methylcyclobutenes.

The results of these calculations are given in Table II together with the experimental values for  $\Delta F^\circ_{25}$  and

(5) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(6) L. S. Bartell and R. A. Bonham, *ibid.*, **32**, 824 (1960).

(7) L. S. Bartell, *ibid.*, **32**, 827 (1960).

(8) J. De Boer, *Physica*, **9**, 363 (1942).

(9) K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956).

(10) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 1071.

(11) A. I. Kitaigorodskii, *Soviet Phys. Cryst.*, **6**, 408 (1962).

Table II. Energy Differences (kcal./mole) between Methyl Isomers

	—Nonbonded interactions (calcd.)—			$\Delta F_{25}^{\circ}$ (obsd.)	$\Delta H_{25}^{\circ a}$	—Nonbonded interactions— (calculated with C-C <sub>exo</sub> = 1.46 Å.)		
			1- and 3-methyl isomers					
Methylcyclobutenes	-0.85 <sup>b</sup>	-1.19 <sup>c</sup>	-0.22 <sup>d</sup>	≈ -5.4		-0.15 <sup>b</sup>	-0.20 <sup>c</sup>	0 <sup>d</sup>
Methylcyclopentenes	-3.15 <sup>b</sup>	-1.91 <sup>c</sup>	-0.54 <sup>d</sup>	-2.8	-3.1	-1.55 <sup>b</sup>	-0.21 <sup>c</sup>	-0.10 <sup>d</sup>
Methylcyclohexenes	...	...	...	-2.4	-2.8	...	...	...
			3- and 4-methyl isomers					
Methylcyclopentenes	-0.46 <sup>b</sup>	-0.41 <sup>c</sup>	-0.18 <sup>d</sup>	-0.13	-0.28			

<sup>a</sup> Calculated from  $\Delta F_{250}^{\circ}$  and  $\Delta F_{25}^{\circ}$  assuming  $\Delta S^{\circ}$  to be constant in this temperature range and  $\Delta H_{25}^{\circ} = \Delta H_{250}^{\circ}$ . <sup>b</sup> Formula A (Table I, Bartell).<sup>7</sup> <sup>c</sup> Formula B (Table I, Kitaigorodskii).<sup>11</sup> <sup>d</sup> Formula C (Table 7, De Boer, Hirschfelder).<sup>8,10</sup>

$\Delta H_{25}^{\circ}$ . The nonbonded interactions stabilize the 1-methyl isomer because the bond angles at the approximately trigonally hybridized C<sub>1</sub> carbon are larger than those at the tetrahedrally hybridized C<sub>3</sub> atom. As the cyclic bond angles increase, a reduction of the nonbonded distances to the C<sub>exo</sub> carbon occurs in both the 1- and the 3-methyl isomers. However, in the 3-isomers the C···C<sub>exo</sub> distances are shorter, and because of the shape of the potential curve, the energy increases more rapidly when the shorter distances are reduced.

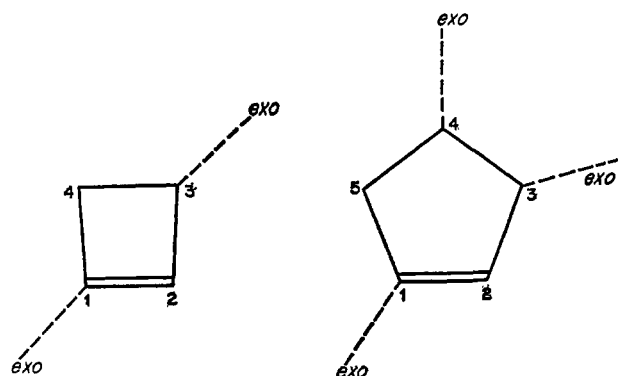


Figure 1. Numbering of carbon atoms in cyclobutenes and cyclopentenes.

In fact, the *calculated*, nonbonded stabilization energies of the 1-isomers increase with increase of the ring size according to all potential functions used. The experimental data on the other hand show a trend in the opposite direction, indicating that nonbonded interactions are not the major cause of the energy differences. These findings in themselves would be an argument for the correctness of the softer De Boer-Hirschfelder potential function; the harder Bartell function, for example, gives a nonbonded interaction stabilization for the methylcyclopentenes which amounts to as much as the total energy difference between the 1- and 3-methyl isomers. However, it will be shown below that the exocyclic C-C bond length in the 1-methyl derivatives must be shorter than 1.54 Å., and such a shortening tends to reduce the stabilization predicted by the functions of Bartell and Kitaigorodskii.

Calculations of the nonbonded interactions in methylcyclohexenes are complicated by the nonplanarity and flexibility of the ring system. An estimate of the difference between these interactions can, however, be obtained indirectly, as shown further below.

(b) According to Dewar and Schmeising the so-called hyperconjugation energy can very well be in-

terpreted as being due to  $\sigma$ -bond stabilization. The effect of methyl substitution on heat of isomerization has been estimated to be about 1.5 kcal./mole in the 1-methyl derivatives of cyclohexene, cyclopentene, and cyclobutene.<sup>12,13</sup>

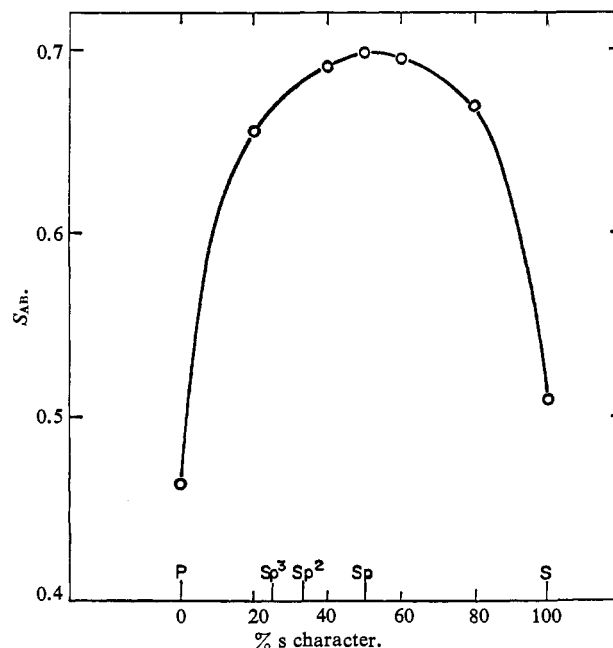


Figure 2. Overlap integral for an  $sp^n-sp^8$  C-C bond of 1.50 Å. length, calculated using Slater orbitals: R. S. Mulliken, C. A. Rieke, D. Orloff, and M. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949). Percentage s character is defined as  $100/(1+n)$ .

The data listed in Table II suggest, however, that this stabilization energy increases with decreasing ring size, and this trend can be understood in terms of change in hybridization of the C<sub>1</sub> and C<sub>2</sub> carbon atoms with decreasing cyclic angles. Coulson and Moffitt<sup>14</sup> have shown that in strained, small-ring cycloparaffins the p-character of the orbitals participating in the cyclic bonds and the s-character of those forming exocyclic bonds increase with a reduction of the cyclic angles (see ref. 15 for pertinent infrared data). A similar effect in the cycloolefins will affect the  $\sigma$ -bond stabilization energy. In general, this energy will be maximal when

(12) R. B. Turner, in "Theoretical Organic Chemistry," IUPAC Kekulé Symposium, Butterworth and Co. (Publishers), London, 1959, p. 79.

(13) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **80**, 1424 (1958).

(14) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(15) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

the exocyclic C-C bond is an  $sp-sp^3$  bond,<sup>16</sup> as further increase of s character reduces overlap (Figure 2) and thereby weakens the bond.<sup>17</sup> It should be noted that the hybridization energy is not sensitive to small deviations from  $sp$  character, since the curve of Figure 2 has a rather flat maximum at per cent  $s = 50$  (corresponding to an  $sp$  orbital).

We can calculate the maximum value of the stabilization energy using the formula of Dewar and Schmeising<sup>2</sup>

$$E_{\max} = [E_{sp-sp^3} - E_{sp^2-sp^3}]_{C-C} - [E_{sp-s} - E_{sp^2-s}]_{C-H}$$

Substitution of values for the bond energies reported in ref. 18 gives  $E_{\max} = 4.9$  kcal./mole, while for an unstrained system in which the exocyclic  $=C-C$  and  $=C-H$  bonds are, respectively,  $sp^2-sp^3$  and  $sp^2-s$  linkages, the calculated hybridization energy is 2.6 kcal./mole. Both these values exclude stabilization due to differences in nonbonded interactions, which were included in a later formula by Dewar and Schmeising,<sup>18</sup> but have been allowed for separately in the present calculations.

In comparing theory with experiment the following assumptions were made. The values of  $\Delta H^\circ_{25}$  in Table I were derived from  $\Delta F^\circ_{25}$  and  $\Delta F^\circ_{250}$  assuming  $\Delta S^\circ$  and  $\Delta H^\circ$  to be constant between 25 and 250°. Further, our calculations give an estimate of  $\Delta H^\circ$  at the temperature of absolute zero, which is compared with  $\Delta H^\circ_{25}$ . Put in other words, we consider the specific heats of the various isomers to be very similar. Published entropy values of methylcyclopentenes in a wide temperature range<sup>19</sup> support this assumption.

Comparison between the calculated energy differences and the  $\Delta H^\circ_{25}$  values listed in Table II shows that for the methylcyclobutenes good agreement with experiment can be obtained only with a hybridization energy close to the maximum value of 4.9 kcal./mole. For the methylcyclopentenes  $\Delta H^\circ_{25}$  is much lower; the experimental value of 3.1 kcal./mole agrees with the sum of the nonbonded interaction difference as calculated with the softer potential functions and a hybridization energy about equal to the normal unstrained value of 2.6 kcal./mole. It is of interest that  $\Delta H^\circ_{25}$  for the methylcyclohexenes is similar to the corresponding value for methylcyclopentenes. Since in the latter compound the hybridization energy is already equal or close to the unstrained value, we may conclude that stabilization due to nonbonded interactions is about the same for the methyl-substituted five- and six-membered olefinic rings.

Thus, the thermochemical data suggest that the exocyclic C-C bond in 1-methylcyclobutene is almost an  $sp-sp^3$  bond, comparable with the C-C bond in methylacetylene. Such a change should be detectable in the infrared spectrum, but C-C stretching bands are relatively weak and have been of limited value for the elucidation of molecular structure.<sup>20</sup> However, the  $=C-H$

bond will be affected in the same sense, though possibly to a lesser extent, since, unlike a carbon  $sp^3$  orbital, the hydrogen s orbital has no directional properties. Some relevant C-H stretching frequencies are given in Table III and it is seen that the pertinent C-H stretching frequency in cyclobutene (and in 1-methylcyclobutene) is indeed intermediate between those of the ethylenic and acetylenic groups.

Table III. Some C-H Stretching Frequencies (cm.<sup>-1</sup>) of Unsaturated Hydrocarbons

(C=)CHR	3040-3010 <sup>a</sup>
(C≡)CH	3300 <sup>b</sup>
Cyclobutene	3126, 3043 <sup>c</sup>
3-Methylcyclobutene	3135, 3055 <sup>d</sup>

<sup>a</sup> L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, p. 34. <sup>b</sup> Bellamy, p. 58. <sup>c</sup> R. C. Lord and D. G. Rea, *J. Am. Chem. Soc.*, **79**, 2401 (1957).

<sup>d</sup> S. Pinchas, E. Gil-Av, J. Shabtai, and B. Altmann, *Spectrochim. Acta*, **21**, 783 (1965).

From this interpretation it follows that the exocyclic C-C bond is shorter than the reported value of 1.54 ( $\pm 0.03$ ) Å,<sup>21</sup> while the C-H bond length, which is less sensitive to changes in hybridization, should be close to the value used. Results of recalculation of the nonbonded interactions, using, tentatively, an exocyclic C-C bond length of 1.46 Å. (corresponding to an  $sp-sp^3$  bond)<sup>2</sup> are given in Table II. The calculated differences between the 1- and 3-methyl isomers are significantly smaller than those calculated before, and none of the potential functions produces results obviously contradicting the experimental data.

Turner<sup>12</sup> has assumed the quasi-hyperconjugation energy to be 1.5 kcal./mole in 1-methylcyclobutene and the corresponding five- and six-membered ring compounds. Subtracting this value from the isomerization energies of the exocyclic-endocyclic olefin pairs he arrives at an estimate of about 3.0 kcal./mole for the strain difference between isomers in four- and five-membered ring systems containing one and two trigonal carbon atoms, respectively.

As we have shown above, the hybridization energies in 1-methylcyclobutene and 1-methylcyclopentene differ by 2.3 kcal./mole, and allowance for this effect leads to an appreciably larger estimate of approximately 5.3 kcal./mole for the difference in strain energies, *i.e.*, it is about 5.3 kcal./mole more difficult to introduce a second trigonal carbon atom in a four-membered ring than in a ring with five carbon atoms. This estimate does not include any effect of nonbonded interactions, which should be relatively small.

*The Equilibrium between 3- and 4-Methylcyclopentenes.* Finally, the equilibrium between the 3- and 4-methylcyclopentenes is only affected by nonbonded interactions, which can be readily calculated with the dimensions and potential functions given above.

However, the observed differences are small and a comparison between theory and experiment is therefore exceptionally sensitive to the assumptions made. Nevertheless, the calculated values are compatible with experimental data (Table II). The 3-methyl isomer has

(21) This value seems too high even for an unstrained ring, where the exocyclic C-C bond should be about 1.51 Å. (corresponding to an  $sp^2-sp^3$  linkage).

(16) In this case both endocyclic C-1 atomic orbitals could be  $sp^3$  hybrids.

(17) C. A. Coulson, "Valence," 2nd Ed., Oxford University Press, London, 1963, p. 209.

(18) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(19) American Petroleum Institute, Research Project 44, Table 18t, Dec. 1957.

(20) R. N. Jones and C. Sanderfly in "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 350.

lower enthalpy because its methyl group is adjacent to a =CH rather than to a purely  $\sigma$ -bonded >CH<sub>2</sub> group. For the ethylcyclopentenes the difference in nonbonded interactions of the two isomers increases,

and the equilibrium is farther shifted toward the 3-ethyl isomer (part I of this series, Table I).<sup>1</sup>

*Acknowledgment.* The authors are indebted to Dr. I. Steinberg and Dr. M. Bikson for helpful discussions.

## Cycloadditions. III. Reactions of $\Delta^2$ -1,2,3-Triazolines with Phenyl Isocyanate and Phenyl Isothiocyanate<sup>1</sup>

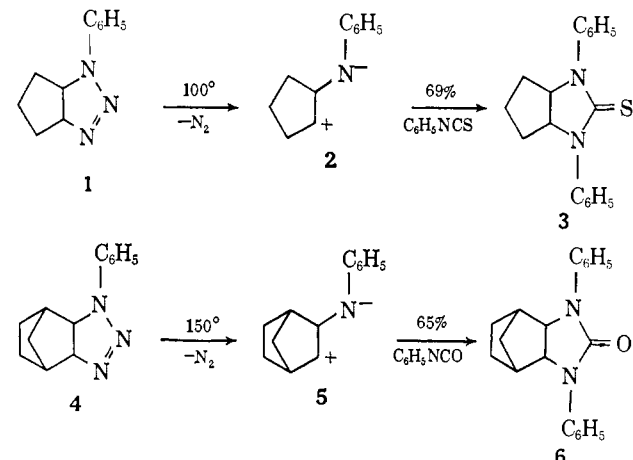
John E. Baldwin, Gary V. Kaiser,<sup>2</sup> and Judith A. Romersberger<sup>2</sup>

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803. Received May 22, 1965

The cyclopentene-phenyl azide adduct and phenyl isothiocyanate react at 110° to give nitrogen and 2-anilino-cyclopentenylthiocarbonyl. The norbornene-phenyl azide adduct and phenyl isocyanate react at 160° to give nitrogen and a 4,10-diphenyl-4,10-diazatricyclo-[4.2.1.1<sup>2,5</sup>]decan-3-one. These reactions, previously<sup>3</sup> thought to give symmetrical thioureas or ureas and interpreted as proceeding via 1,3-dipolar intermediates, are reconsidered mechanistically.

### Introduction

According to the literature,<sup>3</sup> heating the  $\Delta^2$ -1,2,3-triazolines **1** or **4** with phenyl isothiocyanate or phenyl isocyanate leads in high yield to the symmetrical diphenylthiourea **3** or urea **6**. These reactions are held<sup>3</sup> to proceed by thermal decomposition of a triazoline to nitrogen and a 1,3-dipolar intermediate (**2** or **5**), followed by a "1,3-dipolar cycloaddition."



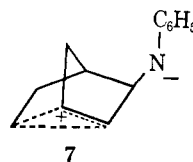
Among the several questions that these reactions and mechanistic conceptions raise, one concerned with the structures of the 1,3-dipolar intermediates **2** and **5**

(1) (a) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society. (b) Cycloadditions. I: J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Am. Chem. Soc.*, **86**, 4509 (1964); II: J. E. Baldwin, *Tetrahedron*, **20**, 2933 (1964).

(2) National Science Foundation Undergraduate Research Participant.

(3) (a) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); **2**, 633 (1963), and references cited therein; (b) R. Huisgen, "Theoretische Chemie und Organische Synthesen," Festschrift der Zehnjahresfeier des Fonds der Chemischen Industrie, Düsseldorf, 1960.

seemed of particular theoretical interest: should the dipolar forms **2** and **5** be taken literally, and/or might they permit product formation corresponding to both rearranged and unrearranged structures? The dipolar form **5** might be imagined particularly capable of leading to rearranged products, insofar as a bridged intermediate<sup>4</sup> such as **7** might be a more adequate representation for the posited intermediate.



A reinvestigation of these reactions was initiated and has produced surprising results: the two reactions give dissimilar products and neither product is a urea. This paper presents evidence for new structural assignments for the products previously reported<sup>3</sup> as **3** and **6**, and attempts to delineate their mechanistic significance.

### 2-Anilino-cyclopentenylthiocarbonyl

When the cyclopentene-phenyl azide adduct, 4-phenyl-2,3,4-triazabicyclo[3.3.0]oct-2-ene (**1**), was heated with an excess of phenyl isothiocyanate in chlorobenzene at 110°, a 78% yield of product C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>S, m.p. 128.5–130.5°, was obtained. That this product, corresponding in molecular formula to an adduct of **2** and phenyl isothiocyanate, could not be formulated as the thiourea **3** was abundantly clear: the product is bright yellow and has  $\lambda_{\text{max}}^{\text{CHCl}_3}$  at 386 m $\mu$  ( $\epsilon$  24,000) and 314 m $\mu$  ( $\epsilon$  9000) in the ultraviolet; its infrared spectrum shows  $\nu_{\text{max}}^{\text{CHCl}_3}$  at 3390, 1612, 1595, 1580, 1500, 1390, and 1250 cm.<sup>-1</sup>; and the n.m.r. spectrum of the product has absorptions at  $\tau$  -3.0 (1 H), 2.0–3.4 (11 H), a multiplet centered at 7.25 (4 H), and a multiplet centered at 8.15 (2 H).

These spectral data were taken as evidence for a 1,2-disubstituted cyclopentene (four allylic protons at  $\tau$  7.25, two nonallylic methylene protons at 8.15) in which the double bond is conjugated with a thio-

(4) For a recent summary and analysis of carbonium ion rearrangements in bridged bicyclic systems, see J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.