Thermal Rearrangements and Cycloaddition Reactions of the *syn*- and *anti*-2-Azatricyclo[4.1.0.0^{3,5}]heptane Ring Systems[1]

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Abstract: *syn-N*-Carbomethoxy-2-azatricyclo[4.1.0.0^{3,5}]heptane (**2a**) rearranges at 121° to give *N*-carbomethoxy-2,3-dihydroazepine (**4a**). *anti-N*-Carbomethoxy-2-azatricyclo[4.1.0.0^{3,5}]heptane (**3a**) also rearranges to give **4a** but much higher temperatures are required. The *anti-N*-methyl derivative undergoes a similar rearrangement to yield the *N*-methyl-2,3-dihydroazepine (**4b**) but at a considerably lower temperature than **3a**. *N*-Phenylmaleimide reacts with the syn isomer **2a** to give cycloadducts **14** and **15**. The anti isomer shows no tendency to undergo cycloadditions. These reactivity differences resulting from the orientational differences of the cyclopropanes are discussed in relation to the existence of an azomethine ylide as an intermediate. An analogy with the heteroquadricyclanes is discussed.

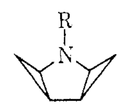
The similarity of the cyclopropane ring system to a double bond in both chemical and physical properties[2] was recognized early in studies on strained molecules. Considerable effort has been expended to increase the comprehension of this analogy. It is known that the interaction of a cyclopropyl substituent with an unsaturated center is dependent on their stereochemical relationship. Theoretical[3] and experimental evidence[4] indicate that the interaction is maximized in conformation **1a** and minimized in conformation **1b**.

1a

1b

From theoretical models that have been used to describe bonding in cyclopropanes it would also be predicted that stereochemistry should be important in regards to the interaction of two cyclopropanes. Although there exists a wealth of data concerning the interaction of cyclopropyl substituents with double bonds and although a number of biscyclopropyl species are known, relatively little work has been published concerning stereochemical requirements for the interaction of two cyclopropane units.[5]

The parent hydrocarbon bicyclopropyl has been shown to exist in the s-trans form in the solid state.[6] However, rotation around the central C–C bond in the liquid and gas phase makes bicyclopropyl a poor choice for conformational reactivity studies. Stereochemically rigid cyclopropanes, such as systems where both cyclopropanes are fused to a small central ring, are more convenient in studying the stereoelectronic effects of two adjacent cyclopropanes. Both the *syn*- and *anti*-2-azatricyclo[4.1.0.0^{3,5}]heptanes (**2** and **3**)



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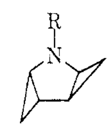

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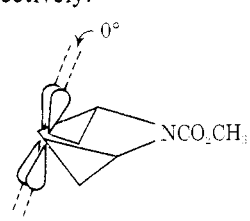
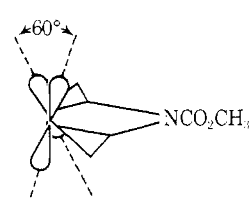
a, $R = CO_2CH_3$
b, $R = CH_3$

meet this requirement. The *N*-carbomethoxy derivatives can be prepared from the cuprous chloride catalyzed decomposition of diazomethane in the presence of *N*-carbomethoxypyrrole, the anti isomer isolated in low yield and the syn isomer isolated only in trace quantities. Both **2a** and **3a** have been previously characterized.[7]

Molecular models indicate that the interaction of the two cyclopropyl groups should be considerably more favorable in **2** than in **3**. Using the Walsh molecular orbital description for cyclopropane,[8] the atomic p orbitals at positions 5 and 6 in the syn and anti isomers form angles of approximately 0 and 60°, respectively.





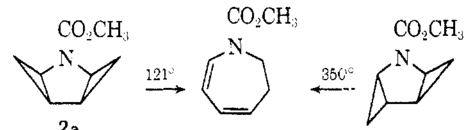
A difference in reactivity between **2a** and **3a** is clearly demonstrated in their thermal rearrangements. Whereas **2a** rearranges at 121° to give the dihydroazepine **4a**, the rearrangement of **3a** requires 350° (Table I).

Table I. Thermal Rearrangements of **2a**, **3a**, and **3b**[a]

Compd	Temp, °C	$k \times 10^5\ \mathrm{sec}^{-1}$
2a	121	3.6
3a	350	3.2
3b	280	44.4

[a] See Experimental Section for details.

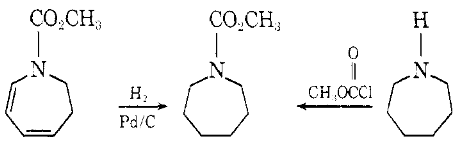
(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.
(2) M. Charton, "The Chemistry of Alkenes," J. Zabicky, Ed., Interscience, New York, N. Y., 1970, Chapter 10, p 511.
(3) For leading references, see (a) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 6592 (1972); (b) W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972); (c) L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, Jr., *ibid.*, **93**, 6948 (1971).
(4) Y. E. Rhodes and V. G. DiFate, *J. Amer. Chem. Soc.*, **94**, 7582 (1972).
(5) For example, see H. A. Corver and R. F. Childs, *J. Amer. Chem. Soc.*, **94**, 6201 (1972).
(6) (a) O. Bastiansen and A. de Meijere, *Acta Chem. Scand.*, **20**, 516 (1966); (b) W. Lüttke and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **5**, 123 (1966); (c) O. Bastiansen and A. de Meijere, *ibid.*, **5**, 124 (1966); (d) J. Eraker and C. Rømming, *Acta Chem. Scand.*, **21**, 2721 (1967).
(7) S. R. Tanny, J. Grossman, and F. W. Fowler, *J. Amer. Chem. Soc.*, **94**, 6495 (1972).
(8) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); see also R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).



2a 4a 3a

The structural assignment of the product of this thermal rearrangement is supported by its spectral data, comparison to the known 2,3-dihydrooxepin[9] and 2,3-dihydroazepine systems,[10] and by the following transformations.

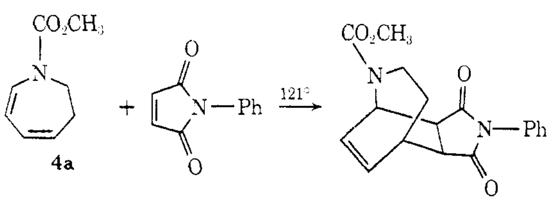
Dihydroazepine **4a** was reduced with hydrogen and 10% palladium on charcoal to give *N*-carbomethoxyhexahydroazepine (**5**) which was independently synthesized by the reaction of hexahydroazepine (**6**) with



4a 5 6

methyl chloroformate in the presence of triethylamine.

Diene **4a**, when heated to 121° with *N*-phenylmaleimide, gave the Diels–Alder adduct **7** as the only



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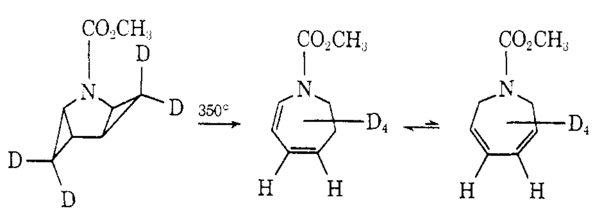
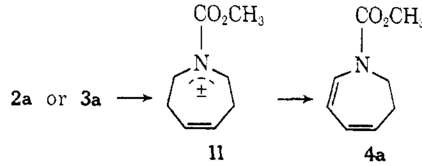
detectable product. Structure **7** is consistent with the spectral and analytical data for the product of this reaction (see Experimental Section).

Heating the tetradeuterio derivative **8**[7] to 350° gave the 2,3-dihydroazepine **9** with the deuterium atoms statistically distributed among positions 2, 3, 6, and 7. This suggests that the dihydroazepine is undergoing rapid 1,5-hydrogen shifts at 350° involving the presumably less thermodynamically stable 2,7-dihydroazepine **10**.



8 9 10

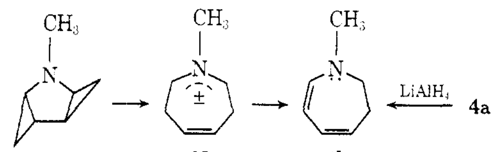
A reasonable mechanism for the thermal rearrangement would involve initial ring opening to dipole **11**



11 4a

which would then undergo an allowed hydrogen shift from position 3 to 7.[11]

The influence of the electron-withdrawing carbomethoxy substituent on the thermal rearrangement of the anti isomer can readily be seen in the thermal rearrangement of the *N*-methyl derivative **3b**. Compound **3b** rearranges to the dihydroazepine **4b** at 280° as compared to the *N*-carbomethoxy derivative **3a** which requires 350°. This greater reactivity of the *N*-methyl derivative is understandable in terms of greater stability being associated with dipole **12** than **11**.[12]



3b 12 4b

The difference in thermal reactivity between **2a** and **3a** can be rationalized by the examination of the transition state leading to **11**. In the syn isomer, **2a**, there is favorable orbital overlap between the atomic orbitals comprising the cyclopropyl bonds that are broken with the atomic orbitals that will ultimately comprise the double bond and azomethine ylide in structure **11**. Therefore, a smooth concerted ${}_{\pi}2_s + {}_{\pi}4_s$ cycloreversion to the dipole can occur. In the anti isomer, **3a**, because of geometrical constraints, only a ${}_{\pi}2_a + {}_{\pi}4_a$ cycloreversion is feasible.[13] In this process, there is not favorable orbital overlap between the atomic orbitals comprising the cyclopropyl bonds that are broken with the atomic orbitals that will ultimately comprise the double bond and azomethine ylide in structure **11**. In the transition state of the thermal rearrangement of the anti isomer **3a** little stabilization will be realized compared to the syn isomer **2a**. Therefore, a greater activation energy for the thermal rearrangement of **3a** would be anticipated.

Clearly, stereoelectronic effects of the two interacting cyclopropyl groups are very important in the thermal rearrangements of **2a** and **3a**. Therefore, we were led to investigate other thermal reactions of these ring systems.

Although the analogy of a cyclopropane with a double bond is well established with respect to many chemical and physical properties, little success has been observed when a cyclopropane is substituted for a double bond in cycloaddition reactions. Diels–Alder reactions where one[14] or both of the double bonds have been replaced by cyclopropanes are extremely rare. For this reason we were led to explore the possibility that **2a** and **3a** might behave as bishomodienes in the Diels–Alder reaction.

Some notable failures of a bis homo Diels–Alder

(9) (a) E. E. Schweizer and W. E. Parham, *J. Amer. Chem. Soc.*, **82**, 4085 (1960); (b) J. Meinwald, D. W. Dicker, and N. Danieli, *ibid.*, **82**, 4087 (1960).

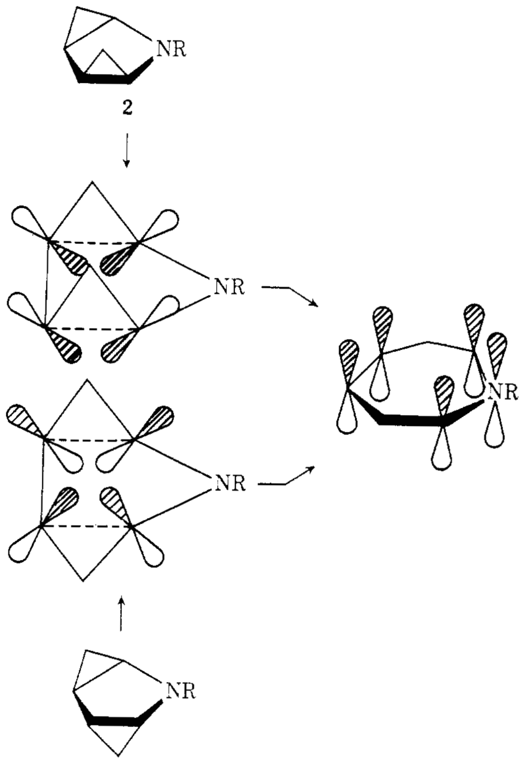
(10) E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Justus Liebigs Ann. Chem.*, **682**, 1 (1965).

(11) This hydrogen shift is electronically analogous to a carbocyclic 1,5-hydrogen shift. Both pass through a six-electron aromatic transition state; see M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(12) For a discussion of 1,3 dipole reactivity, see R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 633 (1963).

(13) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(14) (a) J. E. Baldwin and R. K. Pinschmidt, Jr., *Tetrahedron Lett.*, 935 (1971); (b) S. Sarel and E. Breuer, *J. Amer. Chem. Soc.*, **81**, 6522 (1959); (c) F. W. Fowler, *Angew. Chem., Int. Ed. Engl.*, **10**, 135 (1971); (d) D. J. Pasto and A. Chen, *Tetrahedron Lett.*, 713 (1972).



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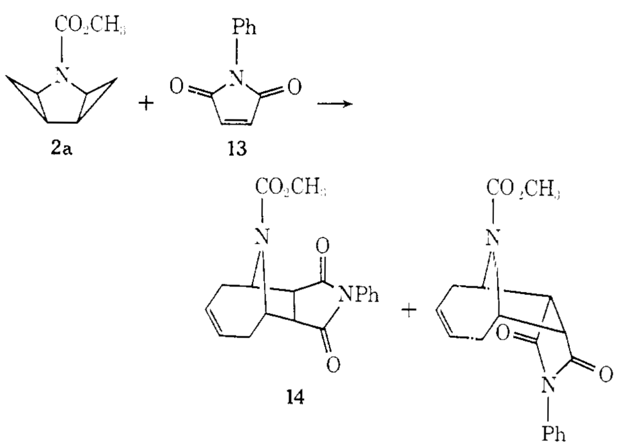
3

reaction are the reaction of dispiro[2.4.2.0]decane with tetracyanoethylene (TCNE) which gave only a product derived from the opening of one cyclopropane ring.[15] Also, it has been reported that 2-phenylbicyclopropyl fails to react with maleic anhydride at 200°.[16]

The only known examples of a bis homo Diels–Alder reaction are with quadricyclane and its derivatives.[17]

Heating **2a** in the presence of 1 equiv of *N*-phenylmaleimide (**13**) for 3 days at 100° produced the two cycloadducts **14** and **15**. Structural assignments were based on spectral data and elemental analyses.

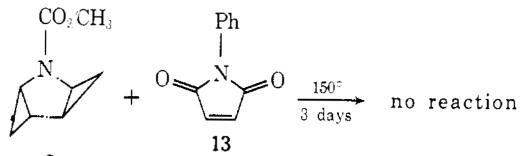


2a **13**

14 **15**

The nmr spectrum of **15** showed important absorptions at τ 4.33 (vinyl hydrogens), 7.26 (allylic hydrogens), 5.14 (bridgehead hydrogens α to nitrogen), and 6.17 (bridgehead hydrogens α to imide carbonyl groups). These assignments were based on observed chemical shifts and double resonance experiments. Exo and endo stereochemistries were assigned by the observation that the hydrogens α to the carbonyls of the imide in **14** show zero coupling in the nmr spectrum with the hydrogens α to the NCO_2CH_3 function while those in **15** are coupled.

In contrast to the reaction of **2a** with *N*-phenylmaleimide, heating the anti isomer **3a** with *N*-phenylmaleimide for 3 days up to 150° showed no loss of starting material.



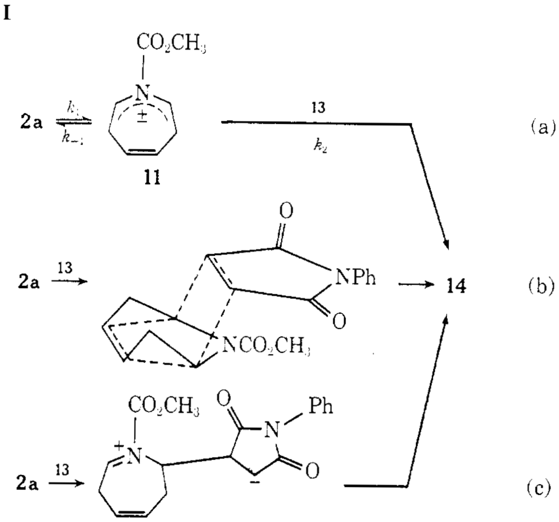
3a **13**

Furthermore, cycloadditions of **3a** and **3b** with a more reactive dienophile such as TCNE were not observed.

Structures **14** and **15** indicate that attack by *N*-phenylmaleimide on the syn isomer **2a** formally occur at positions 1 and 3 of the bishomodiene.

There are several mechanistic possibilities for these cycloadditions, of which three deserve the most consideration (Scheme I). They are: (a) the opening of **2a** to the dipole **11** followed by reaction with *N*-phenylmaleimide to give **14** and **15**, (b) the concerted or nearly concerted cycloaddition passing through a six-membered ring transition state, and (c) the reaction of **2a** with *N*-phenylmaleimide to produce the dipole **16** followed by closure to yield the observed products.

Scheme I



The reaction of **2a** with *N*-phenylmaleimide was found to strictly obey first-order kinetics when up to a five times excess of *N*-phenylmaleimide to **2a** was employed (Table II).

Using the steady-state approximation, the complete kinetic expression for path a in Scheme I is

$$\text{rate} = \frac{k_2[\mathbf{13}]k_1[\mathbf{2a}]}{k_2[\mathbf{13}] + k_{-1}}$$

Although path a can give second-order kinetics ($k_{-1} \gg k_2[\mathbf{13}]$), it is only path a that can display first-order kinetics (when $k_2[\mathbf{13}] \gg k_{-1}$). We conclude that this

(15) D. S. Magrill, J. Altman, and D. Ginsburg, *Isr. J. Chem.*, 7, 479 (1969).

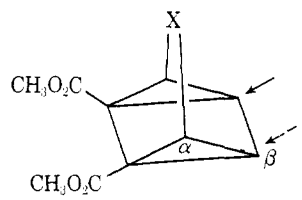
(16) L. I. Smith and E. R. Rogier, *J. Amer. Chem. Soc.*, 73, 3840 (1951).

(17) (a) P. G. Gassman, *Accounts Chem. Res.*, 4, 128 (1971), and references cited therein; (b) I. Tabushi, K. Yamamura, and Z. Yoshida, *J. Amer. Chem. Soc.*, 94, 787 (1972).

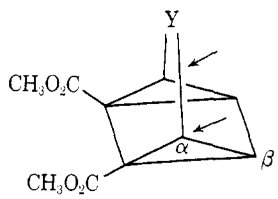
is the most likely mechanism for the cycloadditions of **2a**.

The relative rates of the thermal rearrangement and cycloadditions of **2a** are informative regarding the nature of these reactions. Within experimental error, the rates of these reactions are identical (see Tables I and II). This suggests ring opening to the dipole **11** is the rate-determining step in both reactions.[18] Since none of the thermally rearranged product **4a** is detected (by nmr), it is concluded that the rate of the intermolecular cycloaddition must be faster than the intramolecular hydrogen shift leading to **4a**.

As was mentioned previously, quadricyclane and its derivatives are the only other bishomodienes known to undergo cycloaddition reactions. However, these derivatives show two different modes of reactivity. The carbocycle and its unsaturated derivatives **17** give products that have resulted from attack of the dienophile at the carbon β to the one atom bridge. In contrast, the products derived from cycloadditions on the heterocycles **18** result from attack of the dienophile at the

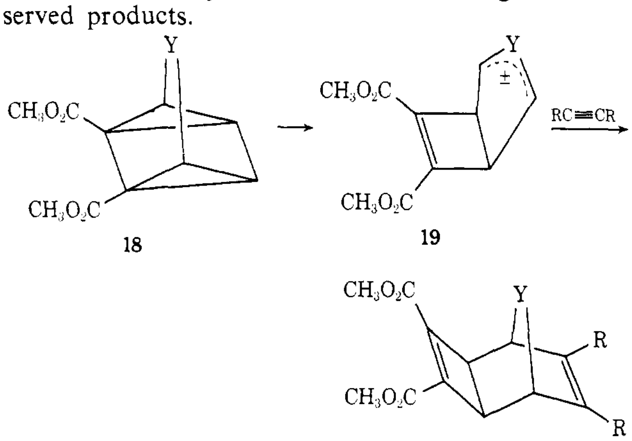


17, X = CH_2, $C(CH_3)_2$, $C{=}C(CH_3)_2$, c-C_3H_6, $C{=}CPh_2$, and $C{=}O$



18, Y = NR and O

carbons α to the one heteroatom bridge.[17a] Our results suggest that the heterocycles **18** possibly first ring open to dipole **19** which then undergoes cycloaddition from the sterically least hindered side to give the observed products.



18 **19** **20**

Table II. Cycloaddition of **2a** with *N*-Phenylmaleimide[a]

Mole ratio of maleimide to **2a**	$k \times 10^5$ sec^{-1} (121°)
1	4.1
5	4.0

[a] See Experimental Section for details.

In contrast to the heterocycles, the carbocycles do not contain nonbonded electrons at position 7 and would gain little by initial ring opening to a dipole (or diradical). An additional bond cannot be formed when the carbocycles **17** undergo a similar ring opening. Therefore, the carbocycles react with a dienophile at the seemingly sterically favorable β position.

From the data we are led to conclude that both cycloadditions and thermal rearrangements of the bishomopyrroles involve dipole intermediates. The heterocycles are formally behaving as bishomodienes in the Diels–Alder reaction, giving products of a 2 + 4 cycloaddition. However, mechanistically the cyclopropanes are not behaving as two-electron components in the Diels–Alder reaction and the heterocycles are not undergoing $4_\sigma + 2_\pi$ cycloadditions. The cycloaddition reaction that gives the product is a $2_\pi + 4_\pi$ cycloaddition involving the dienophile and dipole. The carbocycles **17** are possibly the only systems that are truly behaving as bishomodienes and undergoing $4_\sigma + 2_\pi$ cycloadditions.

These results illustrate again the danger of extrapolating carbocyclic reactivity to heterocycles. Although the reactions might appear similar, they may be proceeding by entirely different mechanistic pathways.

Experimental Section[19]

Thermal Rearrangement of *syn*-*N*-Carbomethoxy-2-azatricyclo[4.1.0.0^{3,5}]heptane (2a). An nmr tube containing 65 mg of **2a** was sealed under argon with nmr grade CCl_4. Heating at 100° for 76 hr produced a 58% yield (vpc triangulation) of *N*-carbomethoxy-2,3-dihydroazepine (**4a**): nmr ($CDCl_3$) τ 3.17 (d, br, 1 H, J = 9.0 Hz), 4.12 (d, 2 H, J = 5.0 Hz), 4.83 (m, 1 H), 6.23 (s, 3 H, OCH_3), 6.26 (m, 2 H), 7.53 (m, 2 H); ir (neat) 3025, 2985 (CH), 1717 (C=O), 1645, 1610 cm^{-1} (C=C); uv (cyclohexane) 277 nm (log ϵ 5.23).

The rate constant determination was performed by the addition of 57 mg of **2a**, nmr grade $CDCl_3$, and 0.25 ml of hexamethyldisiloxane as an internal standard to an nmr tube, flushing with nitrogen, and sealing under vacuum. The tube was heated in an oil bath at 120.9 ± 0.1°, both the disappearance of starting material and appearance of product being observed by nmr. The fitting of points was performed by least-squares analysis with an estimated experimental error of $\pm 0.9 \times 10^{-5}$ sec^{-1}.

Thermal Rearrangement of *anti*-*N*-Carbomethoxy-2-azatricyclo[4.1.0.0^{3,5}]heptane (3a). A 314-ml pyrolysis tube containing 110 mg of **3a** was sealed under vacuum. Heating for 3 hr at 350° produced a 29.6% yield (vpc triangulation) of **4a** identical in every way with that obtained by the thermolysis of **2a**. Further heating for 7 hr at 370° quantitatively converted **3a** to dihydroazepine **4a**. The rate constant for this rearrangement was determined on the basis of a 29.6% yield of **4a** after 3 hr at 350°.

Anal. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.14; O, 20.89. Found: C, 62.47; H, 7.10.

Hydrogenation of *N*-Carbomethoxy-2,3-dihydroazepine (4a) to

(18) Alternative mechanistic pathways for the thermal rearrangement of **2a** to **4a** not involving a common intermediate cannot be completely ruled out. However, in view of the kinetic results discussed above, we believe they cannot play an important role. If the cycloaddition and thermal rearrangement do not involve a common intermediate then the identical rates would have to be coincidental. Since it is unlikely the thermal rearrangement is reversible to any great extent, identical rates for independent pathways would suggest that a mixture of the thermolysis product and cycloaddition products should be produced when **2a** is heated in the presence of *N*-phenylmaleimide. This was not the situation; only the cycloaddition products were detected.

(19) Melting points are uncorrected. The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. The infrared spectra were recorded using a Perkin-Elmer Model 257. The nmr spectra were recorded using a Varian A-60 nmr spectrometer and the JEOL JNM-MH-100 nmr spectrometer.

N-Carbomethoxyhexahydroazepine (5). Initial hydrogenation of 191 mg of N-carbomethoxy-2,3-dihydroazepine (**4a**) with 10% Pd/C produced a mixture of N-carbomethoxyhexahydroazepine (**5**) and N-carbomethoxy-2,3,4,5-tetrahydroazepine as shown by nmr. The N-carbomethoxy-2,3,4,5-tetrahydroazepine was not characterized further. Continuing hydrogenation produced **5** quantitatively: nmr ($CDCl_3$) τ 6.39 (s, OCH_3), 6.64 (m, br, 4 H), 8.48 (s, 8 H); ir (CCl_4) 2929, 2855 (CH), 1700 cm^{-1} (C=O).

Synthesis of N-Carbomethoxyhexahydroazepine (5) from Hexahydroazepine (6) and Methyl Chloroformate. To a 500-ml, round-bottomed flask fitted with a dropping funnel was added 20 g of hexahydroazepine (**6**), 20.5 g of triethylamine, and 200 ml of benzene. The solution was cooled with an ice bath, and, with stirring, a solution of 15.5 ml of methyl chloroformate in 50 ml of benzene was added over a period of 2.25 hr. When the addition was complete, the salts were filtered, the volume was reduced to 90 ml with a rotary evaporator, and the solution was refiltered. Spinning band distillation produced 18.6 g (72% yield based on $ClCO_2CH_3$) of N-carbomethoxyhexahydroazepine (**5**) (bp 120–121° (30 mm)) which was identical in all respects with that obtained by hydrogenation of **4**.

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91; O, 20.36. Found: C, 60.90; H, 9.49.

Synthesis of *anti*-N-Methyl-2-azatricyclo[4.1.0.0^{3,5}]heptane (3b). To 150 mg of $LiAlH_4$ in 10 ml of anhydrous ether cooled with an ice bath was added 153 mg of **3a** with stirring. The reaction was allowed to continue for 28 hr, after which time the excess $LiAlH_4$ was decomposed with 1.0 ml of 20% NaOH. Filtration of salts and removal of the ether by rotary evaporation gave only **3b**: nmr ($CDCl_3$) τ 7.68 (s, 3 H, NCH_3), 7.92 (dt, 2 H, J = 6 Hz, J' = 3 Hz), 8.44 (m, 2 H), 9.63 (m, 4 H); uv (cyclohexane) end absorption only. Structure **3b** was further characterized by conversion to the picrate upon addition to saturated picric acid in ethanol (mp 190° dec).

Anal. Calcd for $C_{13}H_{14}N_4O_7$: C, 46.15; H, 4.17; N, 16.56; O, 33.11. Found: C, 46.09; H, 4.29; N, 16.45.

Thermal Rearrangement of *anti*-N-Methyl-2-azatricyclo[4.1.0.0^{3,5}]-heptane (3b). To a 314-ml pyrolysis tube was added 61 mg of **3b**. Heating at 280° for 0.5 hr gave a 30% yield (vpc triangulation) of N-methyl-2,3-dihydroazepine (**4b**): nmr (CCl_4) τ 4.17 (d, 1 H, J = 9 Hz), 4.48 (m, 2 H), 5.58 (t, 1 H, J = 8 Hz), 6.90 (m, 2 H), 7.22 (s, 3 H, NCH_3), 7.61 (m, 2 H); ir (neat) 2940 (CH), 1597 cm^{-1} (C=C). The rate constant for this rearrangement was determined on the basis of a 30% yield of **10** after 0.5 hr at 280°.

Reduction of N-Carbomethoxy-2,3-dihydroazepine (4a) with $LiAlH_4$. To 123 mg of N-carbomethoxy-2,3-dihydroazepine (**4a**) in 10 ml of anhydrous ether in a 125-ml, round-bottomed flask cooled with an ice bath was added 125 mg of $LiAlH_4$. After 19 hr the reaction was quenched by the addition of 2.0 ml of 15% NaOH. The salts were filtered and the ethereal layer was dried with $MgSO_4$. The ether was removed by rotary evaporation. The nmr showed only N-methyl-2,3-dihydroazepine (**4b**).

Thermal Rearrangement of *anti*-N-Carbomethoxy-4,4,7,7-tetradeuterio-2-azatricyclo[4.1.0.0^{3,5}]heptane (8). Thermolysis of **8** at 375° for 11 hr under conditions identical with the thermolysis of **3a** produced a mixture of N-carbomethoxy-2,3-dihydroazepines **9** with the deuterium atoms statistically distributed over positions 2, 3, 6, and 7. By nmr, position 2 showed $^1/_3$ H; position 3, $^1/_3$ H; 4 and 5, 2 H; 5, $^2/_3$ H; 6, $^2/_3$ H, and NCO_2CH_3, 3 H.

Reaction of N-Carbomethoxy-2,3-dihydroazepine (4a) with N-Phenylmaleimide (13). To an nmr tube was added 95 mg of **4a**, 105 mg of N-phenylmaleimide, 2 drops of hexamethyldisiloxane and enough $CDCl_3$ to record an nmr spectrum. The nmr tube was flushed with nitrogen and sealed under vacuum. After 20 hr at 121°, the nmr showed the reaction to be greater than 90% complete. The adduct **7** was isolated by tlc (silica gel; ether–hexane, 95:5; R_f 0.23) and recrystallized twice from chloroform–pentane: mp 177.5–178.0°; nmr ($CDCl_3$) τ 2.98 (m, 5 H, NPh), 3.90 (m, 2 H, vinyl), 5.07 (m, 1 H), 6.38 (s, 3 H, NCO_2CH_3), 6.11–6.96 (m, 5 H), 8.20 (m, 2 H). In a double resonance experiment irradiation at τ 3.90 caused sharpening at τ 5.07, but had no effect upon the absorption at τ 8.20. Irradiation at τ 8.20 caused simplification of the multiplet at τ 6.11–6.96. The multiplet at τ 6.11–6.96 seems to contain a singlet located at τ 6.86 characteristic of the bridgehead hydrogens α to the carbonyls of the imide when the imide is in the exo position. This fact coupled with the sharp melting point and single spot on a tlc plate allows for tentative identification as the pure exo isomer.

Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.26; H, 5.52; N, 8.59; O, 19.63. Found: C, 66.06; H, 5.32.

Reaction of *syn*-N-Carbomethoxy-2-azatricyclo[4.1.0.0^{3,5}]heptane (2a) with N-Phenylmaleimide (13). To an nmr tube containing 35 mg of **2a** was added 39 mg of N-phenylmaleimide. Heating for 67 hr at 100° gave a 49% yield of the exo cycloadduct **14** and a 40% yield of the endo cycloadduct **15** as determined by nmr. Compounds **14** and **15** were isolated by preparative thin-layer chromotography (silica gel; benzene–ether, 1:3). Exo adduct **14**: nmr τ 2.54 (m, 5 H, NPh), 4.28 (m, 2 H, vinyl), 5.17 (m, 2 H), 6.25 (s, 3 H, OCH_3), 6.86 (s, $W_{1/2}$ = 1.5 Hz, 2 H), 7.18 (m, 4 H); ir (KBr) 3009, 2958 (CH), 1697 (C=O), 1592 cm^{-1} (C=C); mp 163.0–163.5°. Endo adduct **15**: nmr τ 2.55 (m, 5 H, NPh), 4.33 (m, 2 H, vinyl), 5.14 (m, 2 H), 6.17 (m, 2 H, $W_{1/2}$ = 10 Hz), 6.21 (s, 3 H, OCH_3), 7.26 (m, 4 H); ir (KBr) 3003, 2955 (CH), 1696 (C=O), 1588 cm^{-1} (C=C); mp 174.0–175.5°.

In a double resonance experiment on the endo isomer **15** irradiation of the four proton group at τ 7.26 causes the olefinic hydrogens at τ 4.33 to collapse into a singlet. Irradiation of the hydrogens α to the nitrogen at τ 5.14 has no effect on the olefinic hydrogens but causes the four proton group to sharpen.

Anal. Calcd for both isomers $C_{18}H_{16}N_2O_4$: C, 66.26; H, 5.52; N, 8.59; O, 19.63. Found: exo, C, 66.52; H, 5.67; N, 8.39; endo, C, 66.37; H, 5.56.

The cycloaddition rate constant was determined by nmr analysis of a 1:1 and 1:5 molar ratio mixture of **2a** to N-phenylmaleimide in $CDCl_3$ (nmr grade). The samples were purged with N_2, sealed under vacuum, and heated in an oil bath at 120.9 ± 0.1°. In the 1:1 mixture the disappearance of N-phenylmaleimide was followed while in the 1:5 mixture both the disappearance of N-phenylmaleimide and **2a** plus the appearance of products were followed. In both cases, the phenyl protons of N-phenylmaleimide were used as an internal standard. The fitting of points was performed by a least-squares analysis with an estimated experimental error of $\pm 0.9 \times 10^{-6}$ sec^{-1}.

Acknowledgment. The authors wish to express their gratitude to the National Science Foundation for financial support (GP-20099) of this work.