# The Boron Trifluoride Catalyzed Cycloaddition of Iminourethanes with Cyclic Conjugated Olefins. An Examination of Reaction Stereochemistry

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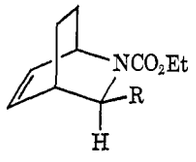
The reaction of formaldehyde bisurethane with five-, seven-, and eight-membered-ring conjugated dienes and cycloheptatriene has been investigated. Bicyclic urethanes are obtained with the seven-membered-ring conjugated systems only; substituted dienes result from both seven- and eight-membered-ring dienes. Reaction products are consistent with a mechanism involving attack by diene on an acid-complexed iminourethane. The stereochemistry of phenyl-substituted bicyclic urethanes synthesized from cycloheptatriene and cyclohepta-1,3-diene using benzaldehyde bisurethane has been determined using nmr with the aid of decoupling experiments. The stereochemical results have been rationalized on the basis of stepwise cycloadditions *via* (*E*)-iminourethanes.

The acid-catalyzed cycloaddition reaction between cyclohexa-1,3-diene and iminocarbamates offers a convenient synthetic route to 3-substituted 5,6-dehydroisoquinuclidines **1**. We have recently reported[1a] on the stereochemical outcome of the synthesis of 3-aryl- and 3-acetyl-5,6-dehydroisoquinuclidines **1b** and **1c** in which predominant formation of the less

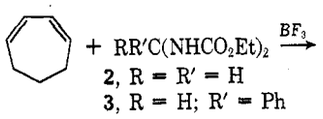


**1a**, R = H
**b**, R = Ph
**c**, R = $COCH_3$

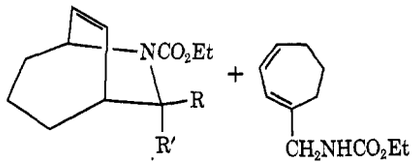
stable 3-exo substituted isomers was found to occur.[1b] We here report an extension of these stereochemical studies to the azabicyclics formed from cyclohepta-1,3-diene and cycloheptatriene, and our observations on the course of the reaction of methylenebisurethane with cyclopentadiene and cyclooctadiene.

**Reaction with Cyclohepta-1,3-diene.**—Methylenebisurethane (**2**) reacts in the presence of boron trifluoride with cyclohepta-1,3-diene[2] to form *N*-carbethoxy-6-azabicyclo[3.2.2]oct-8-ene (**4**) and the addition–abstraction product **5**. Of importance for stereochemical studies on the reaction of substituted iminourethanes with cyclohepta-1,3-diene are the separate nmr (acetone-$d_6$) resonances (Table I) for $H_{7\text{-syn}}$ (δ 3.18) and $H_{7\text{-anti}}$ (δ 3.52) and the unequal couplings $J_{1,7\text{-syn}}$ = 3.2 Hz, $J_{1,7\text{-anti}}$ = 1.6 Hz of these hydrogens with the adjacent bridgehead hydrogen $H_1$. Assignment of the upfield position to the $H_{7\text{-syn}}$ relative to $H_{7\text{-anti}}$ proton can be made on the basis of a previously observed[1a] shielding of the analogous syn proton in the nmr spectrum of *N*-carbethoxy-5,6-dehydroisoquinuclidine (**1a**). The larger vicinal coupling $J_{1,7\text{-syn}}$ is as expected based on the smaller dihedral angle relationship[3] for $H_{7\text{-syn}}$ and $H_1$ as noted in Dreiding models.

Reaction of benzalbisurethane and cyclohepta-1,3-diene afforded a mixture of the epimeric syn (**6**) and anti (**7**) phenyl adducts for which the nmr spectra



**2**, R = R′ = H
**3**, R = H; R′ = Ph

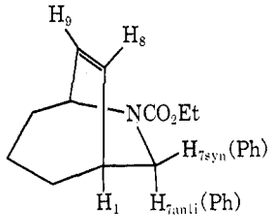


**4**, R = R′ = H
**6**, R = Ph; R′ = H
**7**, R = H; R′ = Ph

**5**

(CDCl₃) are shown in Table I. Notably, $H_8$ in the isomer **6** with phenyl syn to the olefinic bond was shielded by 0.38 ppm relative to $H_9$. This shielding effect by the phenyl substituent on the proximate olefinic hydrogen was noted previously[1a] in the spectra of *syn*-3-phenyl-*N*-carbethoxy-5,6-dehydroisoquinuclidine (**1b**). Spin-decoupling experiments confirmed a 0.26-ppm upfield position for $H_{7\text{-syn}}$ (δ 4.62) of the anti-phenyl isomer **7** relative to $H_{7\text{-anti}}$ (δ 4.88) of the syn-phenyl isomer **6**. As expected from dihedral angle relationships the coupling $J_{1,7\text{-syn}}$ = 4.4 Hz in

TABLE I
100-MHz PROTON NMR PARAMETERS FOR CYCLOHEPTA-1,3-DIENE ADDUCTS



| Compd | Absorption | Chemical shift and description |
|---|---|---|
| **4**[a] | $H_{7\text{-syn}}$ | 3.18 dd ($J_{1,7\text{-syn}}$ = 3.2, $J_{7\text{-syn},7\text{-anti}}$ = 11.2 Hz) |
| | $H_{7\text{-anti}}$ | 3.52 dd ($J_{1,7\text{-anti}}$ = 1.6 Hz) |
| | $H_{8,9}$ | 6.16 m |
| **6** (syn Ph)[b] | $H_{7\text{-ant}}$ | 4.88 d ($J_{7,1}$ = 1.6 Hz) |
| | $H_8$ | 5.80 m |
| | $H_9$ | 6.18 m |
| **7** (anti Ph)[b] | $H_{7\text{-syn}}$ | 4.62 d ($J_{7,1}$ = 4.4 Hz) |
| | $H_{8,9}$ | 6.18 m |

[a] Solvent, acetone-$d_6$. [b] Solvent, $CDCl_3$.

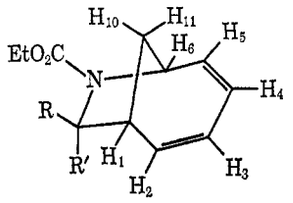
(1) (a) G. Krow and R. Rodebaugh, *J. Org. Magn. Resonance*, **5**, 73 (1973); (b) G. Krow, R. Rodebaugh, R. Carmosin, W. Figures, H. Pannella, G. DeVicaris, and M. Grippi, *J. Amer. Chem. Soc.*, **95**, 5273 (1973); (c) H. Harter and S. Liisberg, *Acta Chem. Scand.*, **22**, 2685 (1968); (d) M. Cava, C. Wilkins, D. Dalton, and K. Bessho, *J. Org. Chem.*, **30**, 3772 (1965).

(2) J. D. Hobson and W. D. Riddell, *Chem. Commun.*, 1180 (1968).

(3) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

TABLE II

100-MHz PROTON NMR SPECTRUM OF THE METHYLENEURETHANE–CYCLOHEPTATRIENE ADDUCTS[a]



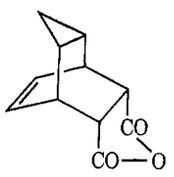

10, R = $H_8$; R′ = $H_9$
11, R = Ph; R′ = $H_9$
12, R = $H_8$; R′ = Ph

| | 10 | | 11 | | 12 | |
|---|---|---|---|---|---|---|
| Absorption | δ | Description | δ | Description | δ | Description |
| $H_1$ | 2.82 | q[b] | 2.62 | m[j] | 3.16 | q[l] |
| $H_2$ | 6.02 | br | 6.16 | m | 5.18 | m[m] |
| $H_3$, $H_4$ | 5.70 | m[c] | 5.74 | m | 5.74 | m |
| $H_5$ | 6.02 | br[d] | 6.16 | m[d] | 6.16 | m |
| $H_6$ | 4.30 | t[e] | 4.57 | t[k] | 4.57 | t[n] |
| $H_8$ | 3.40 | dd[f] | | | 5.08 (5.20)[i] | d |
| $H_9$ | 3.70 | d | 5.26 (5.20)[i] | s | | |
| $H_{10}$ | 2.40 | dt[g,h] | 2.45 | m[g] | 2.45 | m[g] |
| $H_{11}$ | 2.05 | d[h] | 1.92 | d | 2.10 | d |
| $OCH_2$ | 4.00 | br[i] | 3.94 | br[i] | 3.94 | br[i] |
| $CH_3$ | 1.18 (1.20)[i] | t | 0.90 (1.20)[i] | t | 0.90 (1.20)[i] | t |
| Ph | | | 7.15 | m | 7.15 | m |

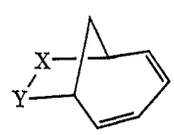
[a] Solvent, acetone-$d_6$. [b] $J_{1,10} \cong J_{1,8} \cong J_{1,2} = 6.0$ Hz. [c] $J_{2,3} = 12$ Hz, $J_{3,5} = 3.5$ Hz. [d] Overlaps with $H_2$. [e] $J_{5,6} \cong J_{6,10} = 7.5$ Hz. [f] $J_{8,9} = 10$ Hz. [g] $J_{10,11} = 12$ Hz. [h] Coupling pattern is observed more clearly in $CDCl_3$. [i] Separate patterns result from separate urethane conformations. [j] $J_{1,9} \cong 0$ Hz, $J_{1,2} = J_{1,10} = 5$ Hz. [k] $J_{5,6} = 7.0$ Hz, $J_{6,10} = 5.5$ Hz. [l] $J_{1,8} = 6$ Hz, $J_{1,2} = J_{1,10} = 7.0$ Hz. [m] $J_{2,3} = 11.5$ Hz. [n] $J_{5,6} = J_{6,10} = 7.0$ Hz.

7 was greater than $J_{1,7\text{-anti}} = 1.6$ Hz of 6. The ratio of syn:anti phenyl isomers was conveniently determined as 1.0 by comparing the integrated area of $H_8$ of the syn-phenyl isomer with the remaining olefinics ($H_{8,9}$ of the anti-phenyl isomer and $H_9$ of the syn-phenyl isomer) or with $H_{7\text{-syn}}$ of the anti-phenyl isomer 7.

**Reaction with Cycloheptatriene.**—In principle reaction of methylenebisurethane with cycloheptatriene might give rise to a number of unusual azabicyclics. Cycloheptatriene forms [4 + 2] adduct **8** by reacting with maleic anhydride *via* the norcaradiene valence tautomer,[4] while the [6 + 2] adducts **9** are found to




8




**9a**, X = Y = O
**b**, X = NSOCl; Y = CO
**c**, X = NPh, Y = O

result from additions of heteroenes, such as chlorosulfonyl isocyanate,[5] nitrosobenzene,[6] and singlet oxygen.[7]

When cycloheptatriene was treated in the usual manner with methylenebisurethane, the single bicyclic adduct **10** was obtained in moderate yield. The structure of **10** can be determined uniquely from the spectral parameters [uv ($CH_3CN$) $\lambda_{max}$ 264 mμ (ε 3760), 240 (3320); ir ($CCl_4$) 1690 $cm^{-1}$] and the nmr spectrum (Table II) in combination with the spin-decoupling technique.

Irradiation of $H_9$ of **10** resulted in a narrowing of the peak width at half-height of $H_{11}$ from 6 to 4 Hz, indicating slight W-plan coupling. The lack of observable coupling $J_{1,11} \cong J_{6,11} \cong J_{9,1} \cong 0$ Hz results from nearly 90° dihedral angle relationships for each of these hydrogen pairs, as can be seen on Dreiding models.

Conformational effects are associated with the urethane functionality, which can have the ethoxyl syn or anti to the adjacent methylene group when in the planar amide conformation,[8] The result is a broadening of the ethoxyl methylene resonance and a separate set of triplet resonances. When $CDCl_3$ was used as solvent, the conformational effect of the urethane resulted in observation of two distinct but partially overlapping resonance patterns for $H_6$, $H_8$, and $H_9$, the protons on carbon adjacent to the nitrogen functionality.

Benzalbisurethane **3** and cycloheptatriene, reacted in the usual manner, afforded benzylurethane **14** (16%) and an epimeric mixture of [6 + 2] adducts **11** and **12** (10%, 80:20, **11**:**12**). The adducts **11** and

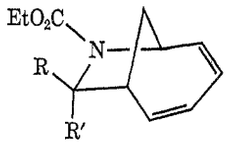
(4) (a) A. S. Onishchenko, "Diene Synthesis," Davey, New York, N. Y., 1964, pp 370–376. (b) D. Bellus, G. Helferich, and C. D. Weiss, *Helv. Chim. Acta*, **54**, 463 (1971). Small amounts of [6 + 2] products occasionally arise, possibly *via* a diradical pathway. (c) H. Ishitobi, H. Tanida, K. Tori, and T. Tsuji, *Bull. Chem. Soc. Jap.*, **44**, 2993 (1971).

(5) (a) E. J. Moriconi, C. F. Hummel, and J. F. Kelly, *Tetrahedron Lett.*, 5325 (1969); (b) J. R. Malpass, *Chem. Commun.*, 1246 (1972).

(6) P. Burns and W. A. Waters, *J. Chem. Soc. C*, 27 (1969).

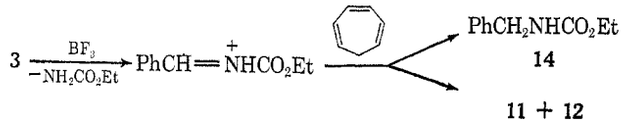
(7) A. S. Kende and J. Y. C. Chu, *Tetrahedron Lett.*, 4837 (1970).

(8) (a) P. T. Inglefield and S. Kaplan, *Can. J. Chem.*, **50**, 1594 (1972); (b) S. VanderWerf and J. Engberts, *Recl. Trav. Chim. Pays-Bas*, **90**, 663 (1971).



**10**, R = R′ = H
**11**, R = Ph; R′ = H
**12**, R = H; R′ = Ph

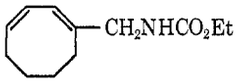
**12** were characterized by uv (EtOH), $\lambda_{max}$ 254 mμ (ε 3900), ir ($CCl_4$), 1695 $cm^{-1}$, and their individual



nmr (acetone-$d_6$) patterns (Table II). Notably in **12** the syn-phenyl group causes an upfield shift for the proximate olefinic proton $H_2$ of 0.98 ppm relative to the remaining olefinic protons, a shift which has also been qualitatively diagnostic for adducts **1b** from cyclohexa-1,3-diene and **6** from cycloheptа-1,3-diene (*vide supra*) where phenyl is syn to the olefinic linkage. In addition a downfield shift of 0.54 ppm for $H_1$ of the syn-phenyl isomer **12** relative to the corresponding $H_1$ proton in the anti-phenyl isomer **11** was observed. This latter shift readily allowed the determination of isomer ratios from the mixture of the two isomers **11** and **12**.

Conformational effects associated with restricted rotation of the urethane functionality and possibly restricted phenyl rotation resulted in broadening of the ethoxyl methylene resonances, and observation of two separate triplet resonances, two singlets for $H_9$ of **11** and two doublets for $H_8$ of **12**. The magnitudes of the separate peaks were strongly effected upon changing the solvent from acetone-$d_6$ to $CDCl_3$. The appearance of $H_6$, the other proton on carbon adjacent to nitrogen, was not perturbed in either of the isomers **11** or **12** in the solvents studied.

**Reaction with Cycloocta-1,3-diene and Cyclopenta-1,3-diene.**—The reaction of dienophiles with cycloocta-1,3-diene has not been found to lead to the formation of bicyclic products.[4a] Similarly, when methylenebisurethane was treated with cycloocta-1,3-diene under the usual conditions, the diene **15** (27%), whose



**15**

structure follows from mechanistic and spectral considerations, was obtained as the only product formed from 1:1 methyleneurethane–diene addition. Although cyclopentadiene reacts readily with a number of dienophilic imines to form azabicyclic molecules,[9,10] reaction of methylenebisurethane with cyclopentadiene under the present acid-catalyzed conditions did not lead to the isolation of 1:1 methyleneurethane–diene adducts.

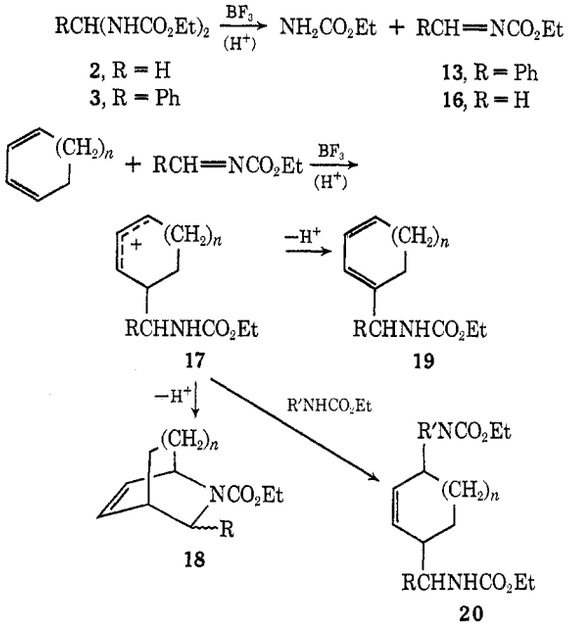
(9) (a) J. Biehler and J. Fleury, *J. Heterocycl. Chem.*, **8**, 431 (1971); (b) G. Kresze and R. Albrecht, *Chem. Ber.*, **97**, 490 (1964).

(10) G. Krow, R. Rodebaugh, J. Marakowski, and K. Ramey, *Tetrahedron Lett.*, 1899 (1973).

## Conclusions

In a previous study[1b] of the reaction of cyclohexa-1,3-diene with alkylidenebisurethanes it was suggested that bicyclic urethane formation was the likely result of a stepwise process (Scheme I) involving acid-com-

SCHEME I



plexed imines.[11] Initial diene addition to the carbon of an acid-complexed iminourethane can form an allylic cation species **17**, which upon intramolecular attack by urethane nitrogen and loss of a proton leads to bicyclic product **18**. Alternatively, the allylic cation can lose a proton to generate a substituted cyclic diene system **19** or be attacked by various urethane species in solution to form less volatile diurethanes **20**. In the present work we have focused our attention on the more volatile monourethane species **18** and **19**.

The present study indicates that formation of substituted dienes **19** assumes importance to a small extent for reactions of cyclohepta-1,3-diene and to a greater degree for reaction of cycloocta-1,3-diene. For the latter, the failure to observe bicyclic urethanes **18** is likely due to conformational strain in assuming the requisite boatlike geometry[12] for intramolecular ring closure of the allylic cation **17**.

The stereochemical results for synthesis of phenyl-substituted azabicyclics are presented in Table III.

TABLE III
STEREOCHEMICAL OUTCOME OF REACTIONS OF CYCLIC DIENES WITH BENZALBISURETHANE[a]

| Diene | Structure | % anti phenyl[b] |
|---|---|---|
| Cyclohexa-1,3-diene | **22** and **23** | 80 |
| Cyclohepta-1,3-diene | **6** and **7** | 50 |
| Cycloheptatriene | **11** and **12** | 79 |

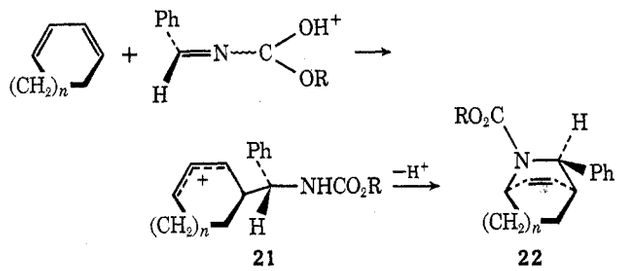
[a] Benzene solvent, $BF_3$ catalyst. [b] Anti relative to the olefinic bridge.

(11) (a) G. Krow, H. Pannella, and W. Figures, *J. Chem. Eng. Data*, **17**, 116 (1972); (b) T. Sasaki, S. Eguchi, M. Sugimoto, and F. Hibi, *J. Org. Chem.*, **37**, 2317 (1972).

(12) A similar problem has been encountered in attempted Diels–Alder cycloadditions to cycloocta-1,3-diene.[4a]

Previously,[1b] two alternative pathways have been suggested consistent with the formation of major amounts of anti-phenyl adducts **22** ($n$ = 1) from cyclohexa-1,3-diene. According to Chart I the observed

CHART I

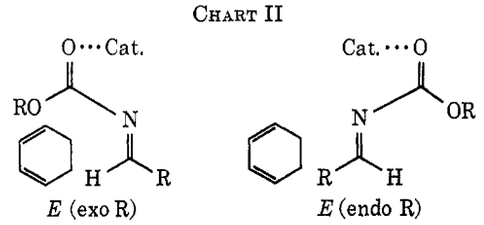


**21** **22**

kinetically derived anti stereochemistry for the phenyl substituent in the formation of **1b** might result from electrophilic attack by iminourethane so that the bulkier phenyl substituent of the imine is oriented toward the less hindered face of the diene. By this argument the imine phenyl substituent will preferentially enter from the side syn to the diene, form a single carbon–carbon bond and allylic cation **21**, and finally collapse following bond rotation to form anti-phenyl product **22**.

For cycloheptatriene initial cationic attack by the complexed imine on the convex face of the triene terminus should be favored with the phenyl group away from the methylene bridge and syn to the olefinic bonds. In order to collapse to product, an initially formed cationic species must undergo a conformational inversion, the result of which locates the rotor substituent in a suitable position for bonding to form the anti-phenyl product **11** of [6 + 2] cycloaddition. Chart II does not explain the failure to observe a

CHART II

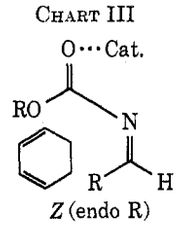


*E* (exo R) *E* (endo R)

preference for the syn-phenyl isomer **7** for reactions of cyclohepta-1,3-diene. Examination of Scheme I might however, provide an answer to this problem. Although initial electrophilic attack may occur with the bulkier substituent oriented over the diene portion of the ring, the initially formed allylic cation **17** can behave in a number of ways. The cation can undergo a rotation and ring closure to form bicyclic amine **18**, it can undergo a conformational inversion whereby the urethane is no longer in a suitable position for intramolecular ring closure and then lose a proton to form a substituted diene **19**, or it can be attacked by external nucleophile to form higher molecular weight material **20**. The final stereochemical course of the cycloaddition would then be the resultant of numerous competing intra- and intermolecular processes. Molecular models indicate that rotation of the substitutent on the allylic cation **17** formed from cyclohepta-1,3-diene is somewhat restricted by the trimethylene bridge. Also, the overall yield of bicyclic adducts **4** (13%) and **6** + **7** (11%), compared to the yields of bicyclic adducts **1** from cyclohexa-1,3-diene (40–50%), indicates the importance of alternative reaction modes for the cation from cyclohepta-1,3-diene.

According to Chart II, a cyclic process might involve cycloaddition of an acid-complexed (*E*)-iminourethane by initial formation of a carbon–carbon bond followed by ring closure. The observed reaction stereochemistry will reflect the relative substituent preferences for the syn position between the substituent on nitrogen and those on carbon of the imine. In the present instance the competition would favor a syn orientation for an acid-complexed urethane functionality which might be attracted to the electron-rich diene. Since steric interaction between the bridge atoms and an anti substituent should vary with the diene employed, variations in reaction stereochemistry may reflect different substituent preferences in the system under investigation. Chart III, involving cy-

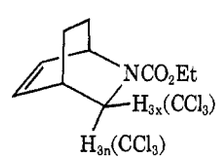
CHART III



*Z* (endo R)

cloaddition of (*Z*)-iminourethanes, is less likely, since the bulkier imine substituents should prefer the sterically less hindered side of the diene leading to a syn adduct preference, which was not observed. For the boron trifluoride catalyzed cycloaddition of the imine from 5-methoxy-3-phenylhydantoin[13] with cyclohexa-1,3-diene, stereospecific formation of syn adduct was observed in agreement with this argument.

Synthesis of *N*-carbethoxytrichloromethylimine[14] and reaction with cyclohexa-1,3-diene afforded 3-trichloromethyl-*N*-carbethoxy-5,6-dehydrosioquinuclidine (**21**), which contained 80% of the *syn*-trichloromethyl



**21a**, exo $CCl_3$
**b**, endo $CCl_3$

isomer.[15] The formation of syn product is best explained by Chart II, in which steric interaction of the bulky trichloromethyl group with the methylene bridge of the diene results in a preference for the less hindered syn orientation. Chart I, on the other hand, should

(13) (a) D. Ben-Ishai and E. Goldstein, *Tetrahedron*, **27**, 3119 (1971). (b) E. Goldstein and D. Ben-Ishai, *Tetrahedron Lett.*, 2631 (1969). (c) We have obtained a single stereoisomer in which the C-3 proton does not exhibit long-range W-plan coupling. This proton is likely anti and the C-3 substituent is thus syn oriented.

(14) H. Ulrich, B. Tucker, and A. Sayigh, *J. Org. Chem.*, **33**, 2887 (1968).

(15) Thermal and acid-catalyzed reactions of halomethylimines with dienes are to be reported elsewhere. Isomer ratios **21a**:**21b** were determined from the nmr resonances (benzene-$d_6$) for $H_{3x}$ ($\delta$ 4.76, d, $J$ = 3 Hz) and $H_{3n}$ ($\delta$ 4.42, q, $J$ = 3, 1.3 Hz).

have led to a preference for the *anti*-trichloromethyl isomer.

In conclusion, the stereochemical course of the present cycloadditions is likely explained as proceeding *via* a stepwise cyclic transition state involving (*E*)-iminourethanes. However, predictions of product structures and stereochemistries based on such a model must be tempered by the recognition that allylic cations may play an important role.

## Experimental Section

The nmr spectra were determined on a Varian Associates XL-100-15 spectrometer using tetramethylsilane (TMS) as an internal standard. Solutions of 5–10% solute in $CCl_4$, $CDCl_3$, or acetone-$d_6$, all containing 1% TMS, were used for nmr measurements. Couplings and coupling constants were where necessary obtained with the aid of decoupling experiments. All vpc work was performed using a 15 ft × 0.25 in., 2% XF-1150 on Chromosorb W column. Stereoisomer ratios obtained by nmr analysis of prepped crude reaction mixtures or distilled material were in agreement.

**General Procedure for the Reaction of Alkylideneurethanes with Dienes.**—A solution of the diene (0.125 mol) in 100 ml of dry benzene was added dropwise over 30 min to a stirred refluxing solution of alkylidenebisurethane (0.125 mol) and 5 g of boron trifluoride etherate in 200 ml of dry benzene. After 8–24 hr reflux the reaction solution was cooled, washed with water, aqueous sodium carbonate, dilute HCl, and water, and dried over magnesium sulfate. After removal of solvent the oil was diluted 10:1 with boiling *n*-heptane, which was then decanted from insolubles. The solvent was then removed *in vacuo* and the product was isolated by distillation and vpc.

***N*-Carbethoxy-6-azabicyclo[3.2.2]non-8-ene (4).**—Cyclohepta-1,3-diene (1.8 g, 0.02 mol) in 15 ml of benzene was added dropwise to a refluxing solution of methylenebisurethane (3.7 g, 0.02 mol) and boron trifluoride etherate (0.5 ml) in 100 ml of dry benzene. Work-up after 18 hr reflux as above afforded 1.45 g of an oil which was distilled (70–72°, 0.01 mm). The bicyclic product (400 mg, 13%) was purified by vpc (145°, retention time 11 min) to separate it from a small quantity of diene **5** (21 min) identified by comparison of its spectral parameters with those reported by Hobson.[2] The bicyclic adduct had spectral parameters ir (film) 1675 $cm^{-1}$, nmr (acetone-$d_6$) $\delta$ 1.58 (b, $H_{2,3,4}$), 2.60 (b, $H_1$), 4.10 ($OCH_2$), 1.20 ($CH_3$); see Table I.

**7-Phenyl-6-azabicyclo[3.2.2]non-8-enes (6 and 7).**—Boron trifluoride etherate (0.5 ml) and benzalbisurethane (13.3 g, 0.05 mol) in dry benzene (250 ml) were heated to reflux and cyclohepta-1,3-diene (4.7 g, 0.05 mol) was added dropwise over 30 min. After 8 hr reflux the reaction mixture was worked up to yield 7.4 g of crude oil which upon distillation (160°, 0.01 mm) afforded 1.5 g (11%) of **6** and **7**: vpc (200°) retention time 10 min; ir (film) 1675 $cm^{-1}$; nmr ($CDCl_3$) for syn-phenyl **6**, $\delta$ 2.65 ($H_1$), 1.68 and 1.28 ($H_{2,3,4}$), 5.00 ($H_5$), 7.18 (Ph), 3.90 ($OCH_2$), 0.84 ($CH_3$), and see Table I; nmr for anti-phenyl **7** $\delta$ 2.65 ($H_1$), 1.68 and 1.28 ($H_{2,3,4}$), 4.92 ($H_5$), 7.18 (Ph), 2.90 ($OCH_2$), 0.84 ($CH_3$), and see Table I. The ratio of anti (**6**) to syn (**7**) isomers as determined by comparison of integrated areas of $H_{7x}$ for the syn-phenyl isomer and $H_8$ of the anti-phenyl isomer was 50:50.

*Anal.* Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.02; H, 7.75; N, 5.28.

***N*-Carbethoxy-7-azabicyclo[4.2.1]nona-2,4-diene (10).**—Boron trifluoride etherate (5.0 g, 0.035 mol) and methylenebisurethane (24.0 g, 0.126 mol) in dry benzene (250 ml) were refluxed and cyclohepta-1,3,5-triene (11.6 g, 0.125 mol) was added dropwise over 30 min. After 8 hr reflux and work-up, distillation afforded 5.5 g (23% yield) of colorless oil **10**: bp 84–87° (0.2 mm); vpc (150°) retention time 9 min; ir ($CCl_4$) 1690 $cm^{-1}$; uv ($CH_3CN$) $\lambda_{max}$ 264 m$\mu$ ($\epsilon$ 3760), 240 (3320); nmr, see Table II. Only viscous tar remained in the distillation pot.

*Anal.* Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.21; H, 7.85; N, 7.42.

**8-Phenyl-*N*-carbethoxy-7-azabicyclo[4.2.1]nona-2,4-diene (11 and 12).**—Boron trifluoride etherate (2.5 g, 0.018 mol) and benzalbisurethane (16.8 g, 0.063 mol) were refluxed in dry benzene (200 ml), and 1,3,5-cycloheptatriene (5.8 g, 0.063 mol) was added dropwise over 30 min. After 8 hr reflux, work-up and distillation of the residue afforded a forerun of benzylurethane **14** (1.8 g, 16% yield), bp 115–120° (0.15 mm), nmr ($CDCl_3$) $\delta$ 7.14, 5.64 (b), 4.2 (d, $J$ = 6 Hz), 4.00 (q, $J$ = 7 Hz), 1.10 (t, $J$ = 7 Hz), identical with an authentic sample prepared from benzylamine and ethyl chloroformate. The product (1.6 g, 10% yield) was obtained as a viscous oil, bp 130–135° (0.15 mm), ir ($CCl_4$) 1695 $cm^{-1}$, uv (EtOH) $\lambda_{max}$ 264 m$\mu$ ($\epsilon$ 3900), nmr, see Table II. The percentage of syn isomer **12** was determined by comparison of the integrated area for $H_1$ of **12** with $H_6$ for both isomers.

*Anal.* Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.65; H, 7.27; N, 5.49.

**Reaction of Methylenebisurethane with Cycloocta-1,3-diene (15).**—Boron trifluoride etherate (0.5 ml) and methylenebisurethane (9.4 g, 0.05 mol) were refluxed in dry benzene (300 ml) containing cupric bromide, and cycloocta-1,3-diene (5.4 g, 0.05 mol) was added dropwise over 30 min. After overnight reflux, work-up afforded a crude oil which upon distillation (130–135°, 0.2 mm) afforded 2.0 g (27%) of diene **18**: vpc (165°) retention time 15 min; ir (film) 1670, 3220 $cm^{-1}$; uv (EtOH) $\lambda_{max}$ 227 m$\mu$ ($\epsilon$ 9000); nmr ($CDCl_3$) $\delta$ 5.6–5.5 (complex olefinic), 5.22 (NH), 4.08 ($OCH_2$), 3.75 ($CH_2N$, $J$ = 6 Hz), 2.12 (allylic), 1.50 (methylene), 1.20 ($CH_3$).

*Anal.* Calcd for $C_{12}H_{19}NO_2$: C, 68.90; H, 9.09; N, 6.70. Found: C, 68.78; H, 9.15; N, 6.71.

**Attempted Reaction of Methylenebisurethane with Cyclopentadiene.**—Reaction of cyclopentadiene and methylenebisurethane as described according to the general procedure did not afford 1:1 diene–methylenebisurethane adducts upon work-up. Only higher molecular weight materials resulted.

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