mp 258–259°. The ir spectrum (KBr) showed absorptions at 3360 (NH), 1650 (amide I), and 1530 cm^{-1} (amide II).

Anal. Calcd for $C_{22}H_{36}Br_2N_2O_2$: C, 50.78; H, 6.97; Br, 30.71. Found: C, 50.95; H, 6.86; Br, 30.49.

3,3'-(1,3-Adamantylene)bis(1-*tert*-butyl-2-aziridinone) (2).— Potassium *tert*-butoxide (0.740 g, 6.60 mmol) was added in one portion to a stirred slurry of 2,2'-(1,3-adamantylene)bis(2-bromo-*N-tert*-butylacetamide) (1.00 g, 1.92 mmol) in 50 ml of dry ether under nitrogen at 0 to −10°. The reaction was monitored by ir. When the reaction was complete (15 min), the mixture was extracted with 100 ml of cold water, and the organic phase was removed and dried over magnesium sulfate. Evaporation of the solvent gave 522 mg (75.8%) of a light yellow solid, mp 119–123°. An analytical sample was prepared by recrystallization from hexane, mp 121.5–123.5°. The ir (CCl$_4$) showed a strong carbonyl at 1835 cm^{-1} and no NH absorption. The pmr (CCl$_4$) showed 1.29 (singlet, 18 H, *tert*-butyl protons), 1.6–2.2 (hump, 14 H, adamantylene protons), and 2.52 ppm (singlet, 2 H, methine protons). The ultraviolet spectra showed (hexane) λ_{max} 252 nm (log ϵ 2.54) and (EtOH) λ_{max} 237 nm (log ϵ 2.85).

Anal. Calcd for $C_{22}H_{34}N_2O_2$: C, 73.70; H, 9.56; N, 7.82. Found: C, 73.55; H, 9.65; N, 7.74.

B. Mass Spectra.—The conventional ("low resolution") mass spectra were recorded on a Hitachi RMU-6D instrument at

Morgan-Schaffer Corporation, Montreal, Canada, at 100° ion source temperature and 40–60° inlet temperature. Metastables were calculated by computer. Final selections were made manually, utilizing intensity data. The metastable-defocusing work was done on an AEI MS-902 instrument. The high resolution spectrum ("element map") was recorded on a CEC 21-110B doubly focusing mass spectrometer in conjunction with an IBM 1801 computer.

Aziridines. XVIII. The Pyrolytic and Iodide Ion Catalyzed Rearrangements of the *cis-* and *trans-*13-*p*-Nitrobenzoyl-13-azabicyclo[10.1.0]tridecanes[1]

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Pyrolysis of *trans-*13-*p*-nitrobenzoyl-13-azabicyclo[10.1.0]tridecane (3) in toluene at 110° gave a mixture of *trans-N-*(2-cyclododecenyl)-*p*-nitrobenzamide (6) and *cis-N-*(2-cyclododecenyl)-*p*-nitrobenzamide (5) in a ratio of 2:1. Pyrolysis of *cis-*13-*p*-nitrobenzoyl-13-azabicyclo[10.1.0]tridecane (4) in xylene at 140° gave a mixture of 6 and *trans-*2-*p*-nitrophenylcyclododecano[4,5-*d*]oxazoline (7) in a ratio of 7:1. Reaction of 4 with sodium iodide in acetone gave *cis-*2-*p*-nitrophenylcyclododecano[4,5-*d*]oxazoline (12). The formation of these products was rationalized in terms of the probable conformations of 3 and 4 and their respective transition states as deduced from the reported conformations of the corresponding aziridinium methiodides found by X-ray studies.

The thermal rearrangement of *N*-aroylaziridines to give unsaturated amides has been studied extensively and found to be in the category of pyrolytic cis eliminations such as the Chugaev reaction and the Cope elimination of tertiary amine oxides.[2-5] In accord with this view, the isomerization of *N*-aroylaziridines fused to carbocyclic rings of 5, 6, 8, and 10 carbon atoms was found to yield only the unsaturated amide incorporating a cis double bond.[6-9] This reaction must occur by way of the transition state 1b. If a trans double bond were to be formed by a cis elimination in such compounds, it would have to occur by way of a transition state such as 1a which obviously would impose a considerable strain on the smaller, less flexible rings, where $n \leq 10$. Furthermore, in such rings a cis double bond is thermodynamically more favorable than the trans. Only when a ring size of 11 carbon atoms is reached does

the trans isomer become the more favorable of the two isomers.[10]

In this connection, it seemed to us that an investigation of the pyrolytic rearrangement of the *cis-* and *trans-*13-aroyl-13-azabicyclo[10.1.0]tridecanes would be of particular interest, since in this instance the carbocyclic ring system would be large enough to accommodate a conformation such as 1a and the resulting *trans-*
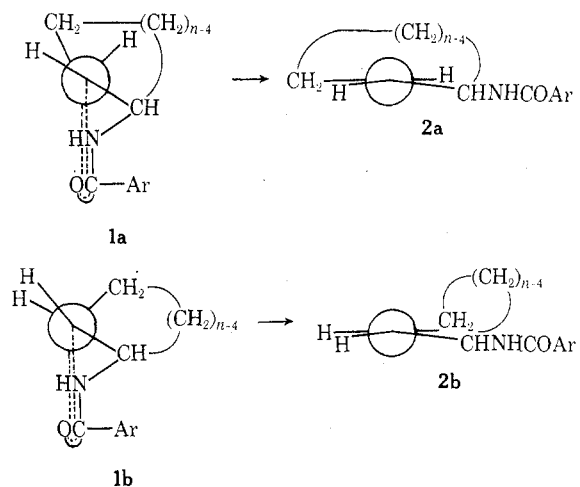
(1) Preliminary work was initiated by B. S. Green and was reported in a Ph.D. Thesis submitted to Illinois Institute of Technology in 1967. The research was completed by I. J. Burnstein and reported in a Ph.D. thesis submitted to Illinois Institute of Technology in 1969. Inquiries should be addressed to P. E. Fanta.

(2) P. E. Fanta and A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958).

(3) P. B. Talukdar and P. E. Fanta, *ibid.*, **24**, 526 (1959).

(4) P. E. Fanta and M. K. Kathan, *J. Heterocycl. Chem.*, **1**, 293 (1964).

(5) D. V. Kashelikar and P. E. Fanta, *J. Amer. Chem. Soc.*, **82**, 4930 (1960).

(6) D. V. Kashelikar and P. E. Fanta, *ibid.*, **82**, 4927 (1960).

(7) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1965).

(8) P. E. Fanta, L. J. Pandya, W. R. Groskopf, and H.-J. Su, *ibid.*, **28**, 413 (1963).

(9) P. E. Fanta, R. J. Smat, and J. R. Krikau, *J. Heterocycl. Chem.*, **5**, 419 (1968).

(10) J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962); J. Sicher, M. Svoboda, B. Mallon, and R. Turner, *J. Chem. Soc. B*, 441 (1968); E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962; J. Zavada, J. Krupicka, and J. Sicher, *Collect. Czech. Chem. Commun.*, **31**, 4273 (1966).

cycloalkene derivative (**2a**, *n* = 12) would not be pro-hibitively strained.

The cis and trans isomers of 13-*p*-nitrobenzoyl-13-azabicyclo[10.1.0]tridecane were prepared in the con-ventional manner from the known *cis*- and *trans*-cyclo-dodecenimines and were found to have the expected infrared and nmr spectral characteristics.

The trans isomer **3** underwent complete thermal iso-merization upon refluxing in toluene at 110° for 48 hr. The crude product was shown by column chromatog-raphy to consist of a mixture containing the *cis*- and *trans*-N-(2-cyclododecenyl)-*p*-nitrobenzamides (**5** and **6**) in a ratio of 1:2.

In contrast, the cis isomer **4** was recovered unchanged after refluxing in toluene solution for 48 hr. It was isomerized by refluxing in xylene at 140° for 72 hr to give a crude mixture which was separated by column chromatography to give the trans unsaturated amide **6**, and the isomeric compound *trans*-2-*p*-nitrophenyl-cyclododecano[4,5-*d*]oxazoline (**7**) in a ratio of 7:1.

The rearrangement products were well characterized by their infrared and nmr spectra. In particular, **6** has an infrared band at 975 cm^{-1} characteristic of *trans* alkenes.[11] In the nmr spectra, **5** and **6** both had bands in the region of τ 4–5, characteristic of the vinyl pro-tons. The coupling constant of the *trans*-vinyl protons in **6** was readily estimated as 14.4 Hz, in agreement with the calculated value of 15.1 Hz for *trans*-cyclododecene.[12] The infrared spectrum of the oxazoline **7** showed no band due to N—H, and has a band at 1645 cm^{-1} at-tributable to C=N. Bands attributable to the bridge-head protons, aromatic protons, and the methylene protons were found in the nmr spectrum of **7**. The re-arrangement product consisting of a mixture of **5** and **6** was further characterized by catalytic hydrogenation to give N-cyclododecyl-*p*-aminobenzamide.
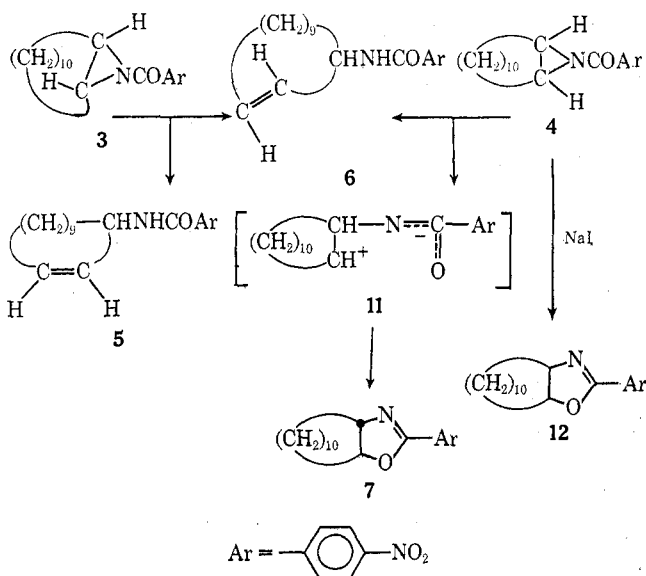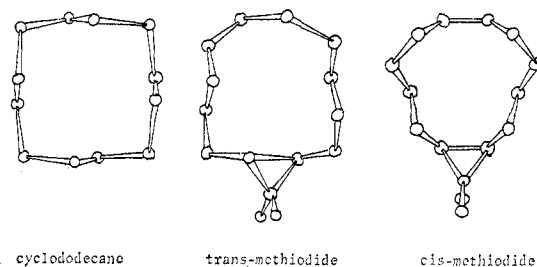
Figure 1.—Favored conformations of cyclododecane deriva-tives.

X-ray diffraction in the laboratory of Trefonas.[13] He found that the conformation of the 12-membered ring in the trans compound closely resembled that previously found by Dunitz for the parent hydrocarbon,[14] while the cis isomer had a completely different conformation, as summarized in the perspective drawings of Figure 1.

If we assume that these conformational preferences are retained in our compounds **3** and **4**, and in the transi-tion states leading to the rearrangement products, the difference in product formation on pyrolysis of **3** and **4** can be convincingly rationalized on stereochemical grounds.

With the aid of Dreiding models, it was found that the *trans*-aroyl derivative **3** can readily assume two conformations in which the carbonyl oxygen approaches either the cis or trans hydrogen on the adjacent methyl-ene group. The change from one conformation to the other is accomplished by a synchronous rotation along the C_1–C_2 bond and the C_{11}–C_{12} bond, with almost no change in the conformation of the remaining part of the cyclododecane ring, as may be seen by inspection of the perspective drawings **8** and **9**. Both conformations are essentially equivalent to the favorable "Dunitz" con-formation of cyclodedecane, and neither appears to be prohibitively strained.

In conformation **8** the carbonyl oxygen approaches the cis proton on the adjacent methylene group. A further extension of this process to the corresponding transition state and to the rearrangement product would lead ultimately to the cis-amide **5**. In conforma-tion **9**, the approach of the carbonyl group is to a trans proton on the adjacent methylene group, which analo-gously would lead to the *trans*-amide **6**.

Furthermore, it may be seen that the transition state from **9** is more favorable than from **8**, because in the former case the hydrogens on the carbon atoms which ultimately form the olefinic bond approach an eclipsed conformation with the methylene and methynyl carbons as shown in Newman projection **1a**. In con-trast, the transition state corresponding to **8** results in a less favorable conformation in which the relatively bulky groups are eclipsed. On this basis, the finding that more **6** than **5** is formed may also be explained.

Examination of the Dreiding model of compound **4** shows that this molecule lacks the flexibility of the trans isomer. The possibility of a rocking motion of the aziridine moiety is absent, and the molecule is particularly rigid in the region of the fusion of the two rings. The carbonyl oxygen can only approach the cis proton on the adjacent methylene group, as shown in

Ar = —⟨benzene ring⟩—NO₂

Discussion

The conformations of the *cis*- and *trans*-13,13-di-methyl-13-azoniabicyclo[10.1.0]tridecane iodides in the crystalline state have been determined by single crystal

(11) L. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 45.

(12) G. Smith and H. Kriloff, *J. Amer. Chem. Soc.*, **85**, 2016 (1963).

(13) L. Trefonas and J. Couvillion, *ibid.*, **85**, 3184 (1963); L. Trefonas, R. Towns, and R. Majeste, *J. Heterocycl. Chem.*, **4**, 511 (1967).

(14) J. Dunitz and H. Shearer, *Helv. Chim. Acta*, **43**, 18 (1960).

the perspective drawing **10**. The other proton is intra-annular and can only be rotated outward by a radical disruption of the conformation of the 12-membered ring. The permitted conformation leads to a transition state which results in the formation only of the *trans* amide **6**, and even the attainment of this transition state seems somewhat less favorable than for conformation **9**.

⟶ *cis*-amide **5**

8

⟶ *trans*-amide **6**
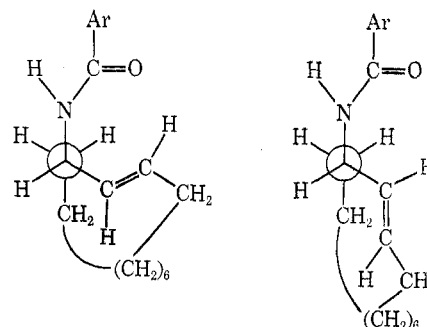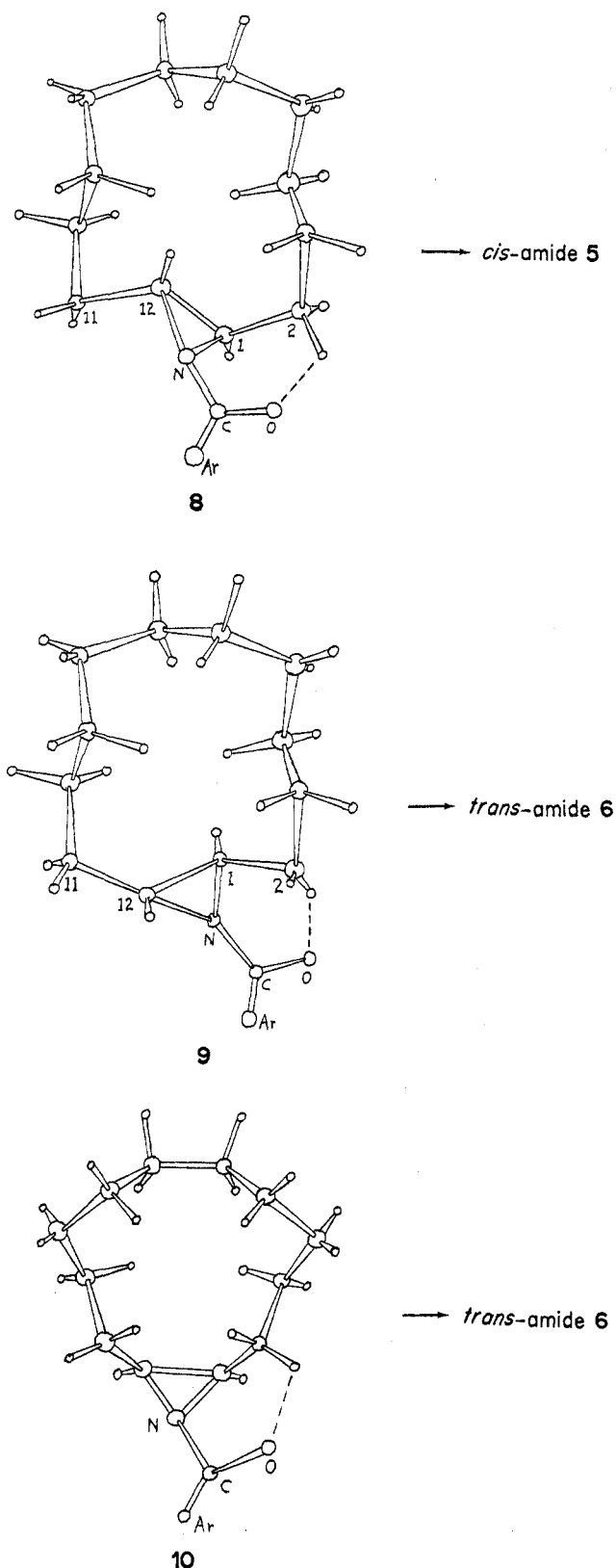
9

⟶ *trans*-amide **6**

10

Figure 2.—Hypothetical diasteromers of *trans*-amide **6**.

Previous studies have shown that an oxazoline is a product of the pyrolysis of *N*-acylaziridines where there are no α hydrogens available, or where the cyclic transition state leading to formation of the unsaturated amide is highly strained.[9] In general, it appears that the higher the temperature required to effect rearrangement, the greater the proportion of oxazoline formed. This is in accord with the supposition that oxazoline formation proceeds by way of a zwitterion intermediate, **11**. Ring closure of the zwitterion **11** occurs to give the *trans*-oxazoline which is thermodynamically the more stable of the two possible isomers.

A careful inspection of the models representing the transition states and final products shows that the rearrangement of **3** and **4** would yield diasteriomeric forms of the *trans*-amide **6**, having the relationship shown in Figure 2. Such a pair of diasteriomers would be interconverted by a 180° rotation about the vinyl carbon–methinyl carbon bond, which is a "flipping through the ring" of the vinyl proton. The fact that we found no evidence of such diasterioisomerism suggests that the rotation occurs freely. Roberts and Binsch have observed that inversion by flipping through the ring occurs in *trans*-cyclodecene, with an activation energy of about 10.7 kcal/mol.[15] In the more flexible 12-membered ring it should occur much more readily.

It is now well known that *N*-acyl aziridines are isomerized by reaction with suitable nucleophiles, such as iodide ion, to give an isomeric oxazoline. The reaction proceeds by two successive nucleophilic substitution reactions of the SN2 type so that retention of configuration is observed when there is the possibility of isomeric oxazolines being formed.[16] Since the reaction involves as a first step the attack of the relatively large iodide ion on the backside of an aziridine carbon atom, it is subject to steric hindrance.

In the case of our trans derivative **3**, no isomerization by sodium iodide took place either in refluxing acetone or acetonitrile after 48 hr. Refluxing for 24 hr in methyl isopropyl ketone (bp 92–96°) gave a dark, tarry substance which could not be identified. Examination of the model of **3** reveals that a backside approach by a nucleophile would require that it occupy a prohibitively hindered intraannular position.

In contrast, the cis isomer **4** underwent isomerization upon refluxing with sodium iodide in acetonitrile for 48 hr. It is obvious from examination of the models that the back-side approach to the aziridine carbon in **4** is

(15) G. Binsch and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5157 (1965).
(16) O. C. Dermer and G. E. Ham, "Ethylenimine and Other Aziridines," Academic Press, New York, N. Y., 1969, p 282.

Table I

Data for 13-Aroyl and 13-Arenesulfonyl Derivatives of cis- and trans-13-Azabicyclo[10.1.0]tridecane

Product	Registry no.	Molecular formula	Mp, °C	Calcd, %			Found, %		
				C	H	N	C	H	N
cis-Benzoyl	26145-82-4	$C_{19}H_{27}NO$	80–84	79.95	9.54	4.99	79.87	9.44	4.76
trans-Benzoyl	26145-81-3	$C_{19}H_{27}NO$	Oil	79.95	9.54	4.99	78.43	9.53	4.32
cis-p-Nitrobenzoyl(4)		$C_{19}H_{26}N_2O_3$	103–107	69.06	7.90	8.48	69.05	7.85	8.65
trans-p-Nitrobenzoyl(3)		$C_{19}H_{26}N_2O_3$	109–111	69.06	7.90	8.48	68.88	8.01	8.19
cis-p-Bromobenzenesulfonyl	26145-83-5	$C_{18}H_{26}NSO_2Br$	138–141	54.00	6.50		53.98	6.48	
trans-p-Bromobenzenesulfonyl	26145-84-6	$C_{18}H_{26}NSO_2Br$	133–134	54.00	6.50		53.76	6.58	

relatively unhindered; therefore it is reasonable to assume that the oxazoline 12, which was the product of the reaction, has the cis configuration. Furthermore, 12 has a melting point 60° lower than 7, and a similar difference in melting points has been reported for the analogous unsubstituted phenyl oxazolines.[17]

Experimental Section

Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and M-H-W Laboratories, Garden City, Mich. Nmr spectra were obtained by use of a Varian A-60 spectrometer on solutions in deuteriochloroform. Infrared spectra were determined in Nujol mulls. Melting points are uncorrected.

cis- and trans-13-Azabicyclo[10.1.0]tridecane.—These imines were prepared as previously described.[18] The cis-imine had a melting point of 87–92° (lit.[18] 85–90°) and the trans-imine melted at 49–52° (lit.[18] 50–55°).

Aroyl and Arenesulfonyl Derivatives of cis- and trans-13-Azabicyclo[10.1.0]tridecane.—The derivatives listed in Table I are all obtained in excellent yield by dropwise addition of a benzene solution of the corresponding acid chloride to a benzene solution of the parent imine in the presence of triethylamine. The benzene solution was filtered and the solvent removed in a vacuum. If the residue was a solid, it was recrystallized from benzene–hexane. The trans-benzoyl derivative was distilled in a short path apparatus, and the trans-p-bromobenzenesulfonyl derivative was further purified by chromatography on Woelm basic alumina.

Pyrolysis of trans-13-Nitrobenzoyl-13-azabicyclo[10.1.0]tridecane (3).—A solution of 2.2 g of compound 3 in 85 ml of toluene was refluxed for 48 hr. Removal of the solvent in vacuum gave 2.1 g of a tan solid that melted at 125–135°. The crude product was chromatographed on Merck reagent neutral alumina starting with petroleum ether–benzene in a ratio of 1:1 and increasing the ratio of benzene until pure benzene was used. Ten equal fractions of eluent were collected. Evaporation of fraction 6 gave pure cis-amide 5: mp 183–185°; nmr (CDCl$_3$) δ 8.0 (q, aromatic), 6.15 (broad, NH) 5.3 (m, vinyl), 1–2 (envelope); ir (Nujol) 3340 (NH), 1640 (C=O), 750, 780 (cis CH=CH).

Anal. Calcd for $C_{19}H_{26}N_2O_3$: C, 69.10; H, 7.78. Found: C, 69.13; H, 7.89.

(17) J. Sicher and M. Svoboda, *Collect. Czech. Chem. Commun.*, **23**, 1252 (1958).

(18) P. E. Fanta, R. Golden, and H.-J. Hsu, *J. Chem. Eng. Data*, **9**, 246 (1964).

Evaporation of fractions 7–10 gave pure trans-amide 5: mp 156–159° after recrystallization from benzene–petroleum ether; nmr (CDCl$_3$) δ 8.0 (q, aromatic), 6.6 (broad d, NH), 5.5 (J = 14.4 Hz, d, trans-vinyl), 1–2 (envelope); ir (Nujol) 3340 (NH), 1640 (C=O), 975 (trans CH=CH).

Anal. Calcd for $C_{19}H_{26}N_2O_3$: C, 69.10; H, 7.78. Found: C, 69.33; H, 8.04. The cis and trans isomers were isolated in a ratio of 1:2.

Pyrolysis of cis-13-Nitrobenzoyl-13-azabicyclo[10.1.0]tridecane (4).—When compound 4 was refluxed in toluene solution for 48 hr, only starting material was recovered. A solution of 1.30 g of compound 4 in 40 ml of xylene was refluxed for 72 hr. The solvent was removed in vacuum and the residue was chromatographed on Merck neutral alumina. Elution with 1:3 petroleum ether–benzene gave oxazoline 7 as a pale yellow solid: mp 168–171°; nmr (CDCl$_3$) δ 8.2 (q, aromatic), 4.2 and 4.6 (bridgehead H), 1.5 (envelope); ir (Nujol) no NH band at 3000–3500, 1645 (C=N).

Anal. Calcd for $C_{19}H_{26}N_2O_3$: C, 69.10; H, 7.78. Found: C, 68.58; H, 8.06.

Continued elution of the chromatographic column with benzene gave a white solid, mp 156–158°, which was shown by mixture melting point and identity of spectra to be identical with the previously obtained sample of trans-amide 6. The oxazoline 7 and trans-amide 6 were isolated in a ratio of 1:7.

N-(Cyclododecyl)-p-nitrobenzamide.—Cyclododecylamine (Aldrich Chemical Co.) in benzene was treated with triethylamine and p-nitrobenzoyl chloride and the reaction worked up in the usual way to give a 60% yield of the expected product: mp 188–191° after recrystallization from ethanol; ir (Nujol) 3310 (NH), 1630 (C=O).

Anal. Calcd for $C_{19}H_{28}N_2O_3$: C, 68.70; H, 8.43. Found: C, 68.80; H, 8.33.

N-(Cyclododecyl)-p-aminobenzamide.—The corresponding nitrobenzamide was hydrogenated at low pressure for 1 hr in alcohol solution using palladium-on-charcoal catalyst. The expected aminobenzamide melted at 184.5–186° after recrystallization from chloroform, ir 3310 and 3350 (NH and NH$_2$).

Anal. Calcd for $C_{19}H_{30}N_2O$: C, 75.50; H, 9.93. Found: C, 75.51; H, 9.84.

The same compound was obtained when the crude mixture from the pyrolysis of compound 3 was hydrogenated in the same way.

Registry No.—3, 26145-76-6; 4, 26145-77-7; 5, cis, 26145-78-8; 6, trans, 26145-79-9; 7, 26145-80-2; N-(cyclododecyl)-p-nitrobenzamide, 26154-37-0; N-(cyclododecyl)-p-aminobenzamide, 26154-38-1.