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THE ABSOLUTE CONFIGURATION OF *trans*-BICYCLO-[6.1.0]NONANE AND ITS 9-PHENYLAZA ANALOGUE

T. ARATANI, Y. NAKANISI AND H. NOZAKI

Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

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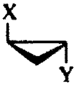
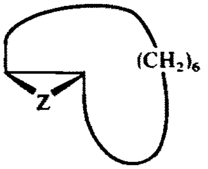
Abstract—The violation of Brewster's rule in (+)(1*R*,8*R*)-*trans*-bicyclo[6.1.0]nonane (**3**) has prompted us to reconfirm the absolute configuration by the following route: (−)(*R*)-*trans*-cyclooctene (**5**) → (+)(1*S*,8*S*)-*trans*-9,9-dibromobicyclo[6.10]-nonane (**13**) → (+)(1*R*,8*R*)-**3**. This assignment establishes the stereospecific *cis* addition of diazomethane to the strained olefin (−)(*R*)-**5** giving (−)(1*R*,8*S*)-*trans*-9,10-diazabicyclo[6.3.0]-undec-9-ene (**6**) rather than (1*S*,8*S*)-*cis* isomer (**9**). Similar stereospecific 1,3-dipolar addition of phenylazide to (−)-**5** produces (+)(1*S*,8*S*)-*trans*-11-phenyl-9,10,11-triazabicyclo[6.3.0]undec-9-ene (**22**), whose photolysis gives (+)(1*S*,8*S*)-*trans*-9-phenylazabicyclo[6.1.0]nonane (**4**). Stereochemical studies have been carried out on the decomposition of bicyclic Δ^1-pyrazoline (**6** and *cis* isomer **9**) to cyclopropane (**3** and *cis* isomer **10**) or that of Δ^2-1,2,3-triazoline (**22** and *cis* isomer **23**) to aziridine (**4** and *cis* isomer **24**), respectively.

INTRODUCTION of substituents X and Y in 1,2 position of a cyclopropane ring gives rise to two diastereomeric pairs of enantiomers and the absolute configuration of *trans* (**1**)[1] and *cis* isomers (**2**)[2] has been established. In continuation of studies on the stereochemistry of cyclopropanes,[2a] we now wish to report the absolute configuration of *trans*-bicyclo[6.1.0]-nonane (**3**) and its 9-phenylaza analogue (**4**). This paper also deals with the stereochemistry of the 1,3-dipolar addition of diazomethane or phenylazide to *trans*- and *cis*-cyclooctene as well as the decomposition of resulting bicyclic Δ^1-pyrazolines or Δ^2-1,2,3-triazolines to cyclopropanes or aziridines, respectively.



(−)-**1a**: X = Y = Me[1a]
(−)-**1b**: X = Y = Ph[1b]
(−)-**1c**: X = Y = COOH[1c]
(−) **1d**: X = Ph, Y = COOH[1c]
(−)-**1e**: X = Me, Y = Ph[1d]
(−)-**1f**: X = Me, Y = COOH[1d]
(−)-**1g**: X = Me, Y = Et[1e]

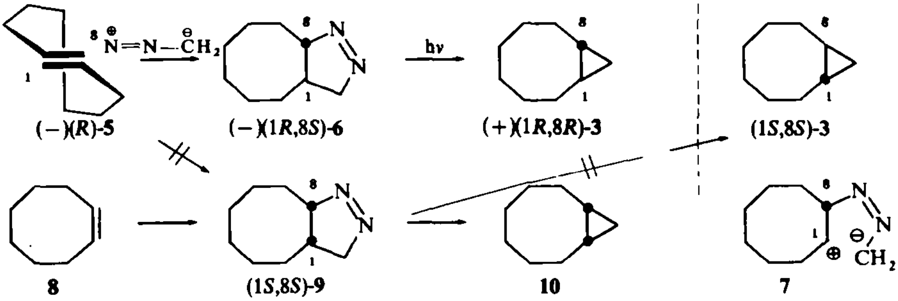
(+)-**2a**: X = Ph, Y = COOH[2a]
(+)-**2b**: X = Ph, Y = Me[2a]
(+)-**2c**: X = Me, Y = COOH[1e, 2a]
(+)-**2d**: X = Me, Y = COMe[2b]
(−)-**2e**: X, Y = —(CH$_2$)$_3$CO—[2c]



(+)-**3**: Z = CH$_2$
(+)-**4**: Z = N-Ph

The absolute configuration of trans-*bicyclo*[6.1.0]*nonane*

Corey and Shulman reported that 1,3-dipolar addition of diazomethane to (−)-*trans*-cyclooctene (**5**) proceeded stereospecifically to give *trans*-fused Δ^1-pyrazoline (−)-**6** and that the photolysis of (−)-**6** afforded (+)-*trans*-bicyclo[6.1.0]nonane **3** stereoselectively.[3] Based on the (*R*) configuration of *trans*-cycloolefin (−)-**5**,[4] the one of *trans*-cyclopropane **3** was deduced to be (+)(1*R*, 8*R*). This assignment forms a marked exception to the Brewster's rule, as the predicted laevorotation ($[M]_D = (-)(X{-}C)(Y{-}C)$) of the (1*R*,2*R*)-*trans* isomer **1** has been the case in all monocyclic compounds ever examined. Although this discrepancy might be attributed to the rigid conformation of the bicyclic system **3**, the steric course leading to (+)(1*R*,8*R*) assignment seemed to require reconsideration from two points of view.



First, the assumed *cis* addition of the 1,3-dipole[5] must be established beyond doubt with respect to so much strained dipolarophile **5**. If the stepwise addition is initiated by electrophilic attack of diazomethane on **5**, the resulting zwitter ion (**7**) can give either *trans*-pyrazoline **6** (retention at C-1) or *cis* isomer **9** (inversion at C-1) according to the relative rates of cyclization and strain releasing rotation.* The second problem is the stereochemistry involved in the conversion of Δ^1-pyrazoline to cyclopropane. *A priori*, *trans*-cyclopropane **3** can be produced either from *trans*-fused **6** (retention at C-8) or *cis*-fused **9** (inversion at C-8). In summary there is no evidence to rule out the possible steric course leading to the opposite assignment: (−)(*R*)-**5** → (−)(1*S*,8*S*)-**9** → (+)(1*S*,8*S*)-**3**.†

We have tried to prepare the novel *cis*-pyrazoline **9** from *cis*-cyclooctene (**8**). A mixture of **8** and diazomethane in ether was left standing for twelve days at room temperature in a pressure bottle. Fractional distillation gave **9** as a colourless oil in as low as 7·6% yield. This sample was shown to be Δ^1-pyrazoline by IR (only N=N stretching at 1555 cm^{-1} and no N—H stretching frequency) and by elemental analyses, but its IR and NMR spectra were clearly different from those of **6** obtained from *trans*-olefin **5** (Experimental). Thus both **6** and **9** were sufficiently pure and no contamination with each other was detected. Further difference was observed in their photochemical behaviour. Irradiation of **9** in hexane with Pyrex-filtered light gave *cis*-bicyclo[6.1.0]nonane (**10**) quantitatively, whereas **6** gave 96% of *trans*-cyclopropane **3** and *cis* isomer **10** (4%). Although these spectral data and photochemical behaviours are already supporting the stereospecific *cis* addition of diazomethane to *trans*- and *cis*-cyclooctene (**5** and **8**) to give *trans*- and *cis*-pyrazoline (**6** and **9**), respectively, final evidence has been obtained by the alternative synthesis of (+)(1*R*,8*R*)-**3**.

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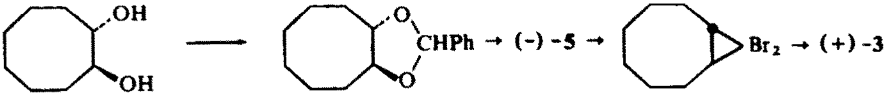
* The 2+2 cycloaddition of benzyne with *trans*-cyclooctene gives 13% of *cis*-1,2-hexamethylenebenzocyclobutene in addition to *trans* isomer (45%), see Ref. 6.

† Corey *et al.* assigned *trans*-configuration **6** for the (−)-pyrazoline on the basis of NMR analysis, see Ref 3.

The optically active *trans*-cyclooctene **5** was prepared by means of Whitham's stereospecific olefin synthesis.[7] The *trans*-cyclooctane-1,2-diol (+)(1*S*,2*S*)-**11**, $[\alpha]_D$ +17·0° (EtOH) or 100% optical purity,[3] was converted to benzaldehyde acetal (+)-**12**, whose treatment with n-butyllithium gave (−)(*R*)-**5**, $[\alpha]_D$ −330° (CH_2Cl_2) or 78% optical purity. Treatment of (−)-**5** with bromoform and potassium *t*-butoxide brought about the stereo-specific *cis* addition of dibromocarbene to give (+)(1*S*,8*S*)-*trans*-9,9-dibromobicyclo[6.1.0]nonane (**13**), $[\alpha]_D$ +34° ($CHCl_3$),* which was reduced with sodium in liquid ammonia to afford (+)(1*R*,8*R*)-**3**, $[\alpha]_D$ +20° (CCl_4 or $CHCl_3$). Thus the violation of Brewster's rule in *trans*-bicyclo[6.1.0]nonane **3**, which is in sharp contrast to monocyclic *trans*-disubstituted cyclopropanes **1**, has been firmly established.†



(+)-**11** (+)-**12** (+)-**13**

The stereochemistry involved in the decomposition of monocyclic and polycyclic Δ^1-pyrazoline derivatives is currently a subject of considerable interest.[8] Crawford *et al.* have studied the decomposition of *trans*- and *cis*-3,4- or 3,5-dimethyl-Δ^1-pyrazolines to *trans*- and *cis*-1,2-dimethylcyclopropane and interpreted the thermolytic results in terms of antisymmetric lowest singlet trimethylene species.[9] Direct photolysis gives floppy excited singlet trimethylene, whereas sensitized photolysis proceeds *via* triplet state of trimethylene.[10] These three modes of decomposition have now been examined with respect to the bicyclic Δ^1-pyrazoline (**6** and **9**) and the results were summarized in Table 1.

TABLE 1. DECOMPOSITION OF 3,4-HEXAMETHYLENE-Δ^1-PYRAZOLINE

Conditions	Pyrazoline	Products, %[a]		
		3 (*trans*)	**10** (*cis*)	Olefins
Thermolysis[b]	**6** (*trans*)	100	0	0
	9 (*cis*)	5	47	49[e]
Direct photolysis[c]	**6** (*trans*)	96	4	0
	9 (*cis*)	0	100	0
Sensitized photolysis[d]	**6** (*trans*)	50	50	0
	9 (*cis*)	7	93	0

[a] Yields were estimated on GLC (PEG-$AgNO_3$, 43°, H_2, TCD).

[b] Decomposition was conducted in sample evaporation chamber (310°) of GLC.

[c] Photolysis of 0·047 *M* hexane solution with Pyrex filtered high pressure Hg arc.

[d] Photolysis of 0·021 *M* benzene solution containing 0·80 *M* benzophenone by means of 366 nm light.

[e] The mixture of methylenecyclooctane (33%) and *cis*-1-methyl-cyclooctene (16%).

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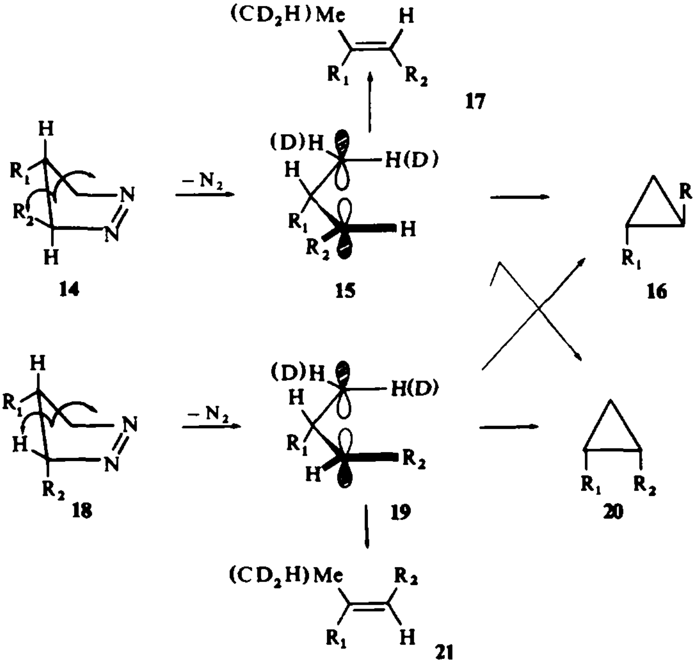
* $[M]_D$ (found) was +96° and $[M]_D$ (calcd) was +300°.

† Chemical correlation of *trans*-bicyclo[n.1.0]alkane (n = 10 and 5) with **3** (n = 6) is now progressing in our laboratory.

The direct photolysis of **6** and **9** produced cyclopropanes (**3** and **10**) almost retaining the configuration of starting materials. Similar tendency has been observed in the photolysis of isomeric 3,4-dimethyl-3-methoxycarbonyl-Δ^1-pyrazoline by Van Auken and Rinehart.[11] Such a specificity was less remarkable in the benzophenone sensitized photolysis to indicate the involvement of triplet trimethylene diradical, which can freely rotate prior to ring closure.

The thermolysis exhibited the notable feature of these bicyclic pyrazolines as compared with the monocyclic ones. In the thermolysis of *trans*- and *cis*-3,4-dimethyl-Δ^1-pyrazoline (**14a** and **18a**) the isomeric 1,2-dimethylcyclopropane (**16a** and **20a**) was formed with no specificity, while 2-methyl-2-butene (**17a** and **21a**) formation was highly specific. Crawford explained these results by assuming the intermediacy of two different antisymmetric singlet trimethylene species: **15a** and **19a**.*

Simple application of this mechanism does not account for our results. Thus *trans*-fused **6** ($\equiv$**14b**) might give rise to trimethylene **15b** favourably affording *cis*-1-methylcyclooctene (**17b**), whereas *cis*-fused **9** ($\equiv$**18b**) might produce more crowded **19b** leading to strained *trans*-1-methylcyclooctene (**21b**). Moreover each antisymmetric species **15b** and **19b** should be able to yield both cyclopropanes, *trans*-fused **3** ($\equiv$**16b**) and *cis*-fused **10** ($\equiv$**20b**). Although the discrepancy between the prediction and the results (Table 1) can not be clearly explained as yet, the predominant retention of configuration found in 9,10-diazabicyclo[6.3.0]undec-9-ene system to bicyclo-[6.1.0]nonane should be emphasized.



a: $R_1 = R_2 = Me$, **b**: $R_1, R_2 = -(CH_2)_6-$.

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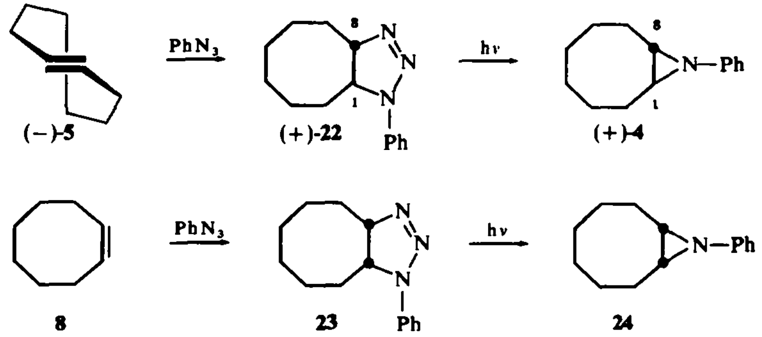
* Both **15a** and **19a** can cyclize in a conrotatory manner to **16a** or **20a**, but hydrogen migration reaction of **15a**–d_2 can only give *trans*-2-methyl-2-butene-1,1-d_2 (**17a**-d_2) and that of **19a**-d_2 can only give *cis*-2-methyl-2-butene-1,1-d_2 (**21a**-d_2), see Ref. 9b.

The absolute configuration of trans-*9-phenylazabicyclo*[6.1.0]-*nonane*

As the *cis* nature of 1,3-dipolar addition to *trans*-cyclo-octene **5** was established in the case of diazomethane, the reaction of phenylazide as another dipole was examined in order to determine the absolute configuration of *trans*-9-phenylazabicyclo[6.1.0]nonane (**4**). The addition of phenylazide to (−)(*R*)-**5**, $[\alpha]_D$ −360° (CH_2Cl_2) or 85% optical purity, took place instantly to give *trans*-triazoline (+)(1*S*,8*S*)-**22**, $[\alpha]_D$ +135° ($CHCl_3$), whose photolysis followed by chromatography on silica gel afforded the desired aziridine **4** in optically active form, $[\alpha]_D$ +117° ($CHCl_3$). Since the *trans* configuration of triazoline **22** was shown as follows, the absolute configuration (1*S*,8*S*) of (+)-**4** was now established.



The diastereomeric *cis*-triazoline **23** was obtained by allowing to stand a mixture of *cis*-cyclooctene **8** and phenylazide for two months. The Δ^2-1,2,3-triazoline structure of both **22** (m.p. 108–109°) and **23** (m.p. 88·5–89·5°) was supported by their spectral data and elemental analyses, and the comparison of their IR and NMR spectra clearly indicated the diastereomeric relationship between **22** and **23** as well as no contamination with each other. These data are consistent with the assigned *trans*

TABLE 2. DECOMPOSITION OF 1-PHENYL-4,5-HEXAMETHYLENE-Δ^2-1,2,3-TRIAZOLINE

Conditions	Triazoline	Products, %[a]		
		4 (*trans*)	**24** (*cis*)	Anil[b]
Thermolysis[c]	**22** (*trans*)	63	18	5
	23 (*cis*)	11	67	22
Direct photolysis[d]	**22** (*trans*)	63	8	4
	23 (*cis*)	2	94	3
Sensitized photolysis[e]	**22** (*trans*)	54	28	3
	23 (*cis*)	10	73	8

[a] Yields were estimated on GLC (HVSG, 178°, N_2, FID) and rest percentage products were not identified.

[b] Cyclooctylideneaniline.

[c] Decomposition was conducted in sample evaporation chamber (310°) of GLC.

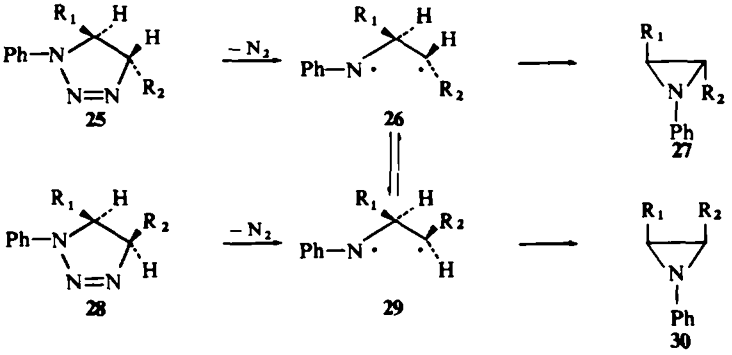
[d] Photolysis of 0·036 M benzene solution with Pyrex filtered high pressure Hg arc.

[e] Photolysis of 0·044 M benzene solution containing 0·87 M triphenylamine by means of 366 nm light.

and *cis* configuration for **22** and **23**, respectively. Further supports were furnished by the decomposition reaction.

In view of the recent publication by Scheiner *et al.* on the decomposition of Δ^2-1,2,3-triazolines,[12] **22** and **23** were subjected to thermolysis, direct photolysis and sensitized photolysis. The results are summarized in Table 2.

Both the thermal and photochemical decomposition of bicyclic triazolines gave aziridines in good yield, but much anil (cyclooctylideneaniline) formation was found in the thermolysis of *cis*-fused **23**. Furthermore the high specificity found in the direct photolysis, i.e. **22** (*trans*) → **4** (*trans*) and **23** (*cis*) → **24** (*cis*), was less remarkable in triphenylamine sensitized photolysis.* Such a difference between direct and sensitized photolysis was observed in 1,5-diphenyl-4-methyl-Δ^2-1,2,3-triazoline system (**25a** and **28a**),[12b] and the Scheiner's explanation based on the multiplicity of 1,3-diradical (**26** and **29**) would be applicable to the present observation as well.



a: R_1 = Ph, R_2 = Me, **b**: R_1, R_2 = $-(CH_2)_6-$
(**25b** ≡ **22** and **28b** ≡ **23**).

EXPERIMENTAL

All b.ps and m.ps are uncorrected. IR spectra were obtained in neat liquid film or as KBr pellets on a Shimadzu IR-27-G spectrophotometer. NMR spectra were taken in 10% CCl_4 solns on a JEOL C-60-H spectrometer and chemical shifts are reported in δ values relative to TMS as an internal standard. Optical rotations were measured with a cell of 5 cm length at room temp (20°).

trans-9,10-*Diazabicyclo*[6.3.0]*undec-9-ene* (**6**). The reaction between *trans*-cyclooctene (1·0 g, 9·1 mmoles) and diazomethane (*ca* 1·0 g) in ether was performed according to the published procedure[13] to give **6** (0·91 g, 66%), b.p. 62°/0·1 mm; IR: 1550, 1445, 1335, 1285, 1095, 910, 890 and 730 cm^{-1}; NMR: δ 0·80–2·30 (m, 12H), 2·80 (m, 1H), 3·60 (octet, 1H), 3·85 (m, 1H) and 4·90 (octet, 1H).

cis-9,10-*Diazabicyclo*[6.3.0]*undec-9-ene* (**9**). A mixture of *cis*-cyclooctene (6·0 g, 55 mmoles) and an ethereal soln of diazomethane (40 ml, *ca* 70 mmoles) was sealed in a pressure bottle and left to stand for 12 days at room temp. Distillation of the reaction mixture under reduced press gave **9** (0·58 g, 7·6%), b.p. 59°/0·1 mm; IR: 1555, 1470, 1450, 1350, 1265, 1160, 1095, 1015, 960, 915 and 745 cm^{-1}; NMR: δ 1·50 (m, 12H), 2·15–2·50 (m, 1H), 3·92 (q, 1H), 4·22 (m, 1H) and 4·53 (q, 1H). (Found: C, 70·8; H, 10·8; N, 18·1. $C_9H_{16}N_2$ requires: C, 71·0; H, 10·6; N, 18·4%).

Photolysis of Δ^1*-pyrazolines* (**6** *and* **9**). A hexane soln (70 ml) of **6** (0·50 g, 3·3 mmoles) in a Pyrex apparatus was irradiated by means of 300 W high press Hg arc for 19 hr, when the quantitative volume of N_2 gas was evolved. The reaction mixture was distilled to give *trans*-bicyclo[6.1.0]nonane (0·35 g, 86%), which was revealed on GLC to be contaminated by a small amount of *cis* isomer (4%). A hexane (50 ml) soln of **9** (0·30 g, 2·0 mmoles) was irradiated as the same manner as above to give *cis*-bicyclo[6.1.0]nonane (0·22 g, 90%), which was free from *trans* isomer on GLC.

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* Irradiation of *trans*-aziridine **4** in the presence of benzophenone or acetophenone caused complete isomerization of **4** to *cis* isomer **24**.

Benzophenone sensitized photolysis of pyrazolines. A benzene soln of benzophenone (0·80 M) and pyrazoline **6** or **9** (0·021 M each) was irradiated for 16 hr by means of 300 W high pressure Hg arc through aq $CuSO_4$ soln (10% w/w). The photolysates were analysed by GLC (Apiezon L 30% on Chromosorb). Under the same irradiation conditions and even in the presence of benzophenone, the isomerization of *trans*-cyclopropane **3** to *cis* isomer **10** could not be detected.

Thermolysis of pyrazolines. A benzene soln (30%) of **6** or **9** was introduced to an injection chamber (310 ± 10°) of GLC and the pyrolysates were analysed directly on GLC (PEG-$AgNO_3$, 43°) by comparison of retention times of products with those of authentic samples: 1-methylcyclooctene,[14] 8·0 min; methylenecyclooctane,[14] 9·5 min; *cis*-bicyclo[6.1.0]nonane, 13·5 min; *trans*-bicyclo[6.1.0]nonane, 15·5 min.

(−)(R)-trans-*Cyclooctene* (**5**). A mixture of (+)-*trans*-cyclooctane-1,2-diol ($[\alpha]_D$ + 17·0° (*c* 2·08, EtOH)[3], 2·0 g, 14 mmoles), benzaldehyde (1·8 g, 17 mmoles) and a small amount of *p*-TsOH in benzene (40 ml) was azeotropically distilled using Dean–Stark trap for 42 hr. Distillation of the reaction mixture gave (+)-10-phenyl-9,11-dioxa-*trans*-bicyclo[6.3.0]-undecane (**12**) (2·9 g, 89%), b.p. 95°/0·06 mm or m.p. 59–60°, $[\alpha]_D$ + 33·2° (*c* 2·02, $CHCl_3$). A mixture of the acetal (+)-**12** (2·9 g, 12·5 mmoles) and a hexane soln of *n*-BuLi (38 ml, 28 mmoles) in petroleum ether (b.p. 40–45°, 38 ml) was stirred at room temp for 18 hr under N_2 atmosphere. After the reaction mixture was treated with water, the organic layer was washed and dried on Na_2SO_4. Evaporation of solvent followed by distillation *in vacuo* through a Vigreux column gave (−)-**5** (0·30 g, 22%), b.p. 40–41°/25 mm, $[\alpha]_D$ −330° (*c* 0·780, CH_2Cl_2) or 78% optical purity based on 425°. The IR spectrum was identical with that of racemic sample.

(+)(1S,8S)-trans-*9,9-dibromobicyclo*[6.1.0]*nonane* (**13**). Bromoform (1·37 g, 5·4 mmoles) was added to a mixture of the olefin (−)-**5** ($[\alpha]_D$ −330°, 0·20 g, 1·8 mmoles) and potassium *t*-butoxide (1·08 g, 7·2 mmoles) in hexane (10 ml) at −10° ~ −15°, and stirring was continued for 3 hr. The reaction mixture was treated with water and extracted with ether. After evaporation of solvents, distillation *in vacuo* gave (+)-**13** (0·28 g, 56%), b.p. 97–98°/5 mm or m.p. 51–52°, $[\alpha]_D$ +34·0° (*c* 1·60, $CHCl_3$). IR: 1165, 995 and 725 cm^{-1}.

(+)(1R,8R)-trans-*Bicyclo*[6.1.0]*nonane* (**3**). An etheral soln of the dibromide (+)-**13** ($[\alpha]_D$ +34°, 0·26 g, 0·93 mmole) was added to a soln of sodium (0·23 g, 10 mmoles) in liquid ammonia at −60° ~ −70°. After stirring for 3 hr, the reaction mixture was quenched with ammonium chloride (0·53 g, 10 mmoles). Work-up followed by distillation and preparative GLC gave a pure sample of (+)-**3** (5 mg, 5%), $[\alpha]_D$ +20° (*c* 0·10, CCl_4 or $CHCl_3$). The IR spectrum was superimposable on that of racemic modifications.

trans-*11-Phenyl-9,10,11-triazabicyclo*[6.3.0]*undec-9-ene* (**22**). A mixture of *trans*-cyclooctene (0·50 g, 4·5 mmoles) and phenylazide (0·60 g, 5·0 mmoles) in ether (10 ml) was stirred for 2 hr at room temp. The resulting precipitate was filtered and recrystallized from benzene to give **22** (0·76 g, 73%), m.p. 108–109° (lit.[15] m.p. 111°); IR: 1600, 1495, 1320, 1090, 1055, 1000, 955, 740 and 690 cm^{-1}; NMR: δ 1·00–2·75 (m, 12H), 3·55 (m, 1H), 4·20 (m, 1H) and 7·15 (m, 5H); UV(EtOH): λ_{max} 286 nm (ε 8500) and λ_{max} 231 nm (ε 7300). (Found: C, 73·6; H, 8·5; N, 18·1. Calc. for $C_{14}H_{19}N_3$: C, 73·3; H, 8·4; N, 18·3%).

cis-*11-Phenyl-9,10-11-triazabicyclo*[6.3.0]*undec-9-ene* (**23**). A mixture of *cis*-cyclooctene (4·4 g, 40 mmoles) and phenylazide (4·8 g, 40 mmoles) was sealed in a pressure bottle under N_2 and allowed to stand for 2 months at room temp. After addition of hexane (20 ml) to the reaction mixture, the separating ppt was filtered. Recrystallization from benzene gave **23** (4·3 g, 43%), m.p. 88·5–89·5 (lit.[15] m.p. 87°); IR: 1600, 1495, 1340, 1320, 1110, 1090, 1065, 1030, 935, 755, 690 and 670 cm^{-1}; NMR: δ 1·00–2·75 (m, 12H), 4·00 (m, 2H) and 7·15 (m, 5H); UV (EtOH): λ_{max} 305 nm (ε 8400) and λ_{max} 289 nm (ε 8630). (Found: C, 73·2; H, 8·4; N, 18·4. Calc. for $C_{14}H_{19}N_3$: C, 73·3; H, 8·4; N, 18·3%).

Photolysis of triazolines (**22** *and* **23**). A benzene soln of **22** or **23** (0·035 M each) in Pyrex apparatus was irradiated by means of 300 W high pressure Hg arc for 18 hr to evolve the quantitative volume of N_2 gas. After distillation *in vacuo*, the photolysate was analyzed on GLC (HVSG 10% on Celite 545, 2 m).

Triphenylamine sensitized photolysis of triazolines. A benzene (0·5 ml) soln of **22** or **23** (1·0 mg each) and triphenylamine (53 mg) in Pyrex apparatus was irradiated by means of 300 W high pressure Hg arc through aq $CuSO_4$ soln (10% w/w) for 7 hr, and the photolysates were analysed on GLC (HVSG 10%, 2 m, N_2, FID). When a benzene soln of *trans*-aziridine **4** and triphenylamine (1 :50 molar ratio) was separately irradiated under the same conditions as above, no isomerization of **4** to *cis*-aziridine **24** was detected. On the other hand, the complete isomerization was observed in the presence of benzophenone or acetophenone.

Thermolysis of triazolines. A benzene soln (30%) of **22** and **23** was heated in an injection chamber (310°) of GLC and the products were analysed directly on GLC.

(+)(1S,8S)-trans-*11-Phenyl-9,10,11-triazabicyclo*[6.3.0]*-undec-9-ene* (**22**). A mixture of (−)-*trans*-cyclooctene ($[\alpha]_D$ −360° (*c* 0·466, CH_2Cl_2), 0·18 g, 1·6 mmoles) and phenylazide (0·19 g, 1·6 mmoles) in ether (5 ml) was stirred for 2 hr. Separating ppt was filtered and washed with a small amount of hexane to give

(+)-**22** (0·23 g, 65%), m.p. 110–115°, $[\alpha]_D$ +135 (*c* 0·310, $CHCl_3$). IR spectrum was superimposable on that of the racemic sample. (Found: C, 73·2; H, 8·2; N, 18·4. Calc. for $C_{14}H_{19}N_3$: C, 73·3; H, 8·4; N, 18·3%).

(+)(1S,8S)-trans-9-*Phenylazabicyclo*[6.1.0]nonane (**4**). A benzene (25 ml) soln of (+)-**22** ($[\alpha]_D$ +135°, 0·21 g, 0·92 mmole) was directly irradiated as described above and the photolysate was purified by column chromatography on silica gel (benzene–ether) to give (+)-**4** (0·10 g, 53%), b.p. 110°/2 mm, $[\alpha]_D$ +117° (*c* 1·23, $CHCl_3$); IR: 1600, 1495, 1460, 1310, 1230, 1210, 1170, 940, 920, 760 and 695 cm^{-1}; NMR: δ 0·50–2·60 (m, 14H) and 6·90 (m, 5H). (Found: C, 83·7; H, 9·6; N, 7·0. $C_{14}H_{19}N$ requires: C, 83·5; H, 9·5; N, 7·0%).

cis-9-*Phenylazabicyclo*[6.1.0]nonane (**24**). The direct photolysate of *cis*-triazoline **23** was purified by column chromatography on basic alumina (benzene–ether (5:2)) to give a pure sample of **24**, b.p. 99–100°/3 mm or m.p. 36–37°; IR: 1600, 1495, 1275, 1220, 1160, 930, 750, 715, 690 and 530 cm^{-1}. NMR: δ 1·00–2·50 (m, 14H) and 6·90 (m, 5H). (Found: C, 83·6; H, 9·4; N, 6·6. $C_{14}H_{19}N$ requires: C, 83·5; H, 9·5; N, 7·0%).

Cyclooctylideneaniline. A mixture of cyclooctanone (0·20 g, 1·6 mmoles), aniline (0·15 g, 1·6 mmoles) and conc HCl (0·01 ml) in toluene (20 ml) was refluxed for 34 hr with continuous removal of water by Dean–Stark trap. Distillation gave the anile (0·20 g, 58%), b.p. 120°/2 mm; IR: 1650, 1605, 1500, 1280, 750 and 700 cm^{-1}.

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