

isolation procedure, 440 mg (85%) of 1-(2,3-dibromo-3-phenylpropionyl)-3-chloroacetyl-4-phenyl-2-pyrazoline: mp 183–185° (recrystallized from methanol); δ (CDCl₃) 4.1–4.7 (m, 3), 4.7 (s, 2), 5.63, 5.88 (dd, 2, AB, |J_{AB}| = 11.5 Hz), 7.2–7.5 (m, 10).

Anal. Calcd. for C₂₀H₁₇Br₂ClN₂O₂: C, 46.86; H, 3.34. Found: C, 46.92; H, 3.49.

3-Methoxyacetyl-4-phenyl-2-pyrazoline (5).—A solution of 1.07 g of **3** in 20 ml of methanol was treated with 2 ml of 1 *N* methanolic hydrochloric acid. After gas evolution ceased, the solution (two spots on tlc) was diluted with water. After extraction, etc., evaporation of the ether gave 260 mg of colorless crystals, mp 115–118°. Two recrystallizations from ether-petroleum ether gave needles of **5**: mp 120–122°; ν_{KB} , 1650 cm⁻¹; δ (CDCl₃) 3.4 (s, 3), 3.4–4.5 (m, 3), 4.5 (apparent doublet, 2-Hz separation, probably center of AB dd), 6.8 (s, 1, NH), 7.2 (s, 5).

Anal. Calcd. for C₁₂H₁₄N₂O₂: C, 66.03; H, 6.59; N, 12.84. Found: C, 65.84; H, 6.25; N, 12.94.

3-Chloroacetyl-4-phenyl-2-pyrazoline (6).—To a solution of 1.07 g of **3** and 2.1 g of LiCl in 10 ml of THF and 5 ml of water was added 4.5 ml of 1 *N* hydrochloric acid. The two-phase mixture was stirred for 2 hr and then extracted, etc. Evaporation gave 0.8 g of white solid still containing an ir peak at 2080 cm⁻¹. Crystallization from ether-pentane gave crystals of **6**: mp 97° (darkening at 60°); one spot tlc (corresponding to faster moving spot in tlc of reaction mixture from **5**); δ (CDCl₃) 3.3–4.5 (m, 3), 4.5 (apparent doublet, 6.75 (s, 1, NH), 7.2 (s, 5). Analytically pure material was not obtained since prolonged drying caused decomposition.

Anal. Calcd. for C₁₁H₁₁ClN₂O: C, 59.33; H, 4.98; N, 12.58. Found: C, 59.82; H, 4.92; N, 12.12.

The hydroxyacetylpyrazoline **7** was prepared from **3** in aqueous THF plus 1 *N* sulfuric acid. A viscous oil was obtained. After purification on a 20 × 20 cm, 2-mm-thick silica gel plate (CHCl₃-MeOH 23:2), the product remained an oil. Treatment with phenyl isocyanate gave the *N*-phenylcarbamate ester of 1-*N*-phenylcarbamoyl-3-hydroxyacetyl-4-phenylpyrazoline: mp 257°; ν_{KB} , 3100, 1720, 1660 cm⁻¹.

Anal. Calcd. for C₂₅H₂₂N₄O₄: C, 67.86; H, 67.86; H, 5.01; N, 12.66. Found: C, 67.65; H, 5.16; N, 12.44.

Registry No.—**2**, 24265-71-2; **3**, 24265-72-3; **4**, 24265-73-4; **5**, 24265-74-5; **6**, 24265-75-6; 1-cinnamoyl-3-chloroacetyl-4-phenyl-2-pyrazoline, 24265-76-7; 1-(2,3-dibromo-3-phenylpropionyl)-3-chloroacetyl-4-phenyl-2-pyrazoline, 24265-77-8; *N*-phenylcarbamate ester of 1-*N*-phenylcarbamoyl-3-hydroxyacetyl-4-phenylpyrazoline, 24265-78-9.

Reaction of 6,6-Dihalobicyclo[3.1.0]hexanes with Morpholine¹

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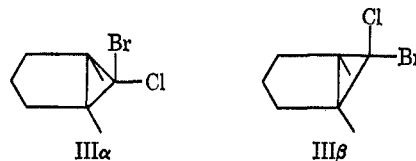
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No reports appear in the literature covering the reaction of *gem*-dihalobicyclo[3.1.0]hexanes with amines to give *N*-substituted derivatives. This report describes the reactions of morpholine with the 6,6-dibromo- (I), 6,6-dichloro- (II), and 6-bromo-6-chlorobicyclo[3.1.0]hexanes (III) at 128°.

Compound I readily reacted with morpholine at 128° in 5 min to give a heavy precipitate of morpholine hydrobromide and 2-bromo-3-morpholinocyclohexene

(IV). Compound II had to be heated for 24 hr before reacting entirely to give 2-chloro-3-morpholinocyclohexene (V).

Compound III exists in two isomeric forms, α and β .



In an earlier brief report² it was indicated that the α and β isomers react stereospecifically with aqueous silver nitrate to give from one isomer only silver chloride and 2-bromo-3-hydroxycyclohexene and from the other isomer only silver bromide and 2-chloro-3-hydroxycyclohexene.

It was now of interest to determine whether these isomers again would exhibit the same stereospecificity in their reaction with morpholine and to determine the products of this reaction.

Compound III was prepared by adding dibromochloromethane to a mixture of cyclopentene and potassium *t*-butoxide at 0°. Crude III was purified by vacuum distillation at temperatures low enough to avoid thermal rearrangement^{3,4} to the bromochlorocyclohexenes. The ir spectrum and bromine unsaturation tests indicated the absence of unsaturation.

Reaction of III with refluxing morpholine (118°) for 5 min gave an exothermic reaction and the precipitation of morpholinehydrobromide. Quenching of the reaction with water and neutralizing with hydrochloric acid afforded 46% V and 32% the less reactive isomer III β . The rapid reaction of the reactive isomer of III with morpholine was similar to the reactivity of I under identical conditions.

The unreactive isomer was obtained by fractional distillation and its purity was ascertained by the vpc and ir and nmr spectra. The ir spectrum of the unreactive isomer lacked the following peaks present in the mixture of isomers: 10.52, 10.87, 11.77, 12.75, and 13.33 μ . Further spectral details are described in Table I. The nmr of the unreactive isomer also lacked a peak at δ 2.05 which was present in the nmr of the mixture of III α and III β . Reaction of this isomer with morpholine at 128° gave no immediate reaction as determined by vpc analysis. After 24 hr the reaction was complete and afforded 62% IV. The reactivity of this isomer was similar to the reactivity of II with morpholine.

In the study of the epimeric 7-chlorobicyclo[4.1.0]heptanes, Cristol and coworkers⁵ suggested that the loss of the halide ion *trans* to the hydrogen atoms at C-2 and C-4 is preferred by a large factor. Schleyer⁶ has observed a similar order of reactivity in the solvolysis of the epimeric monotosylbicyclo[4.1.0]heptanes. Cristol further reasoned that, on the basis of the rates of solvolysis (carried out at 124.6° in glacial acetic acid-sodium acetate), the same halogen leaves in 7,7-bicyclo[4.1.0]heptane.

(2) P. S. Skell and S. R. Sandler, *J. Amer. Chem. Soc.*, **80**, 2024 (1958).

(3) S. R. Sandler, *Chem. Ind. (London)*, 1481 (1968).

(4) S. Winstein and J. Sonnenberg, *J. Org. Chem.*, **27**, 748 (1962).

(5) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Amer. Chem. Soc.*, **87**, 4007 (1965).

(6) P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(1) For the previous paper on the reaction of *gem*-dibromocyclopropanes with morpholine, see S. R. Sandler, *J. Org. Chem.*, **33**, 4537 (1968).

TABLE I
ELEMENTAL AND SPECTRAL ANALYSIS OF THE NEW PRODUCTS

Compound	Calcd, %		Found, %		Nmr spectral data, ^a δ
	C	H	C	H	
III (α and β)	36.80	4.09	37.07	4.30	Complex at 1.85, 2.05, and 2.15 (CH ₂ and CH groups in the cyclopentane ring)
III β	36.80	4.09	36.98	4.27	Complex at 1.85 and 2.15 (CH ₂ and CH groups in the cyclopentane ring)
IV	50.09	6.78	49.91	6.62	Complex at 1.75 and 1.95 (CH ₂ groups in cyclohexene ring) complex at 3.2 (>CHN-), complex at 6.2 (-CH=CBr), and characteristic absorption for the morpholine hydrogens
V	59.50	7.94	59.83	7.94	Complex at 1.68 and 2.0 (CH ₂ groups in the cyclohexene ring), complex at 3.15 (>CHN-), complex at 5.94 (-CH=CBr), and characteristic absorption for the morpholine hydrogens

^a The integrated spectra were consistent with the assigned structure.

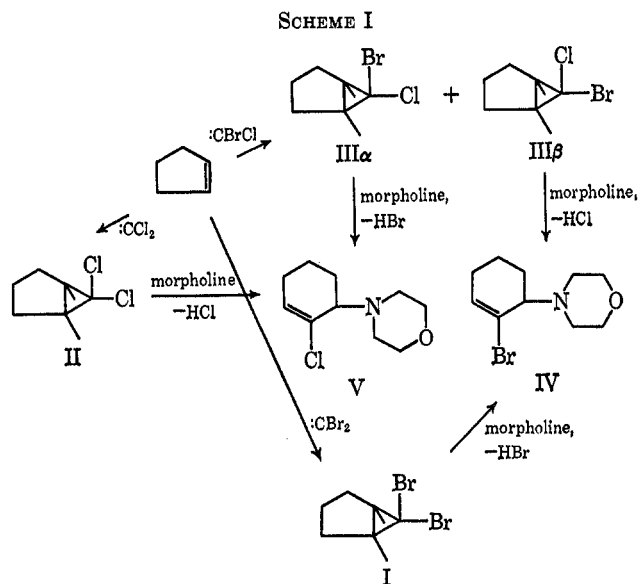
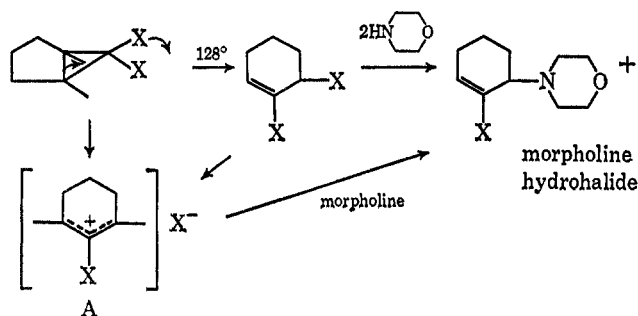
TABLE II
THE THERMAL RING-OPENING REACTION OF
6,6-DIHALOBICYCLO[3.1.0]HEXANES IN THE PRESENCE OF MORPHOLINE

<i>gem</i> -Dihalocyclopropane	Morpholine, mol	Temp, °C	Time, hr	Product ^a	Yield, %	Bp (mm), °C	<i>n</i> _D
I (0.100)	0.200	128	0.25	IV	100	132 (4.0)	1.5383 (20°)
II (0.177)	0.400	128	24	V	45	118 (4.0)	1.5141 (25°)
III α and III β (0.120)	0.240	128	1/12	V	46	88 (0.5)	1.5178 (25°)
				Unreacted isomer (III β)	32	35 (1.0)	1.5241 (25°)
III β , (0.0368, unreactive isomer)	0.200	128	24	IV	62	95 (0.5)	1.5360 (26°)

^a The glpc analyses of the products were obtained on an 8.5-ft column packed with 25% silicone DC 200 on Celite at concentration *P* obtained from The Burrell Corp., Pittsburgh, Pa.

The above data suggests that the stereochemical assignment of the reactive isomer is III α . This isomer should lose Br⁻ at a rate similar to that of I, whereas the unreactive isomer III β should lose a Cl⁻ at a rate similar to that of II. These conclusions are in line with the observed rates of these isomers.² The experimental data is briefly summarized in Scheme I.

Possible mechanisms of this reaction may either involve prior thermal ring opening at 128° to β -haloallyl halides which subsequently react with morpholine to give the observed products or the intermediate for-



mation of carbonium ion A which undergoes a nucleophilic attack by morpholine.

Strong evidence exists in the literature^{4,7} to support the thermal ring opening reaction of I and other *gem*-dihalocyclopropanes.³

Experimental Section⁸

The dihalocarbene adducts were generally prepared by a procedure similar to those described earlier.⁹⁻¹¹ The procedure for the thermal ring-opening reaction of substituted *gem*-dihalocyclopropanes in the presence of morpholine is similar to that described in a previous paper.¹ The preparation of III has not been described before and is briefly given below.

6-Bromo-2-chlorobicyclo[3.1.0]hexane (III).—To a cooled (0–10°) flask containing 27.2 g (0.40 mol) of cyclopentene, 150 ml of pentane, and 33.6 g (0.30 mol) of potassium *t*-butoxide was added dropwise 41.70 g (0.20 mol) of dibromochloromethane (Dow). After the addition the reaction was stirred for 2–3 hr at room temperature, water was added, and the organic layer was separated, washed, dried, and concentrated. The residue upon vacuum distillation yielded 65% III, bp 53° (2.0 mm), n_D^{25} 1.5257–1.5298. The analysis and spectral data is described in Table I.

Tables I and II describe the details of the thermal ring-opening reaction of 6,6-dihalobicyclo[3.1.0]hexanes with morpholine at 128°.

Registry No.—Morpholine, 110-91-8; I, 2568-36-7; II, 23595-96-2; III α , 23595-97-3; III β , 23595-98-4; IV, 23595-99-5; V, 23596-00-1.

Acknowledgment.—The author wishes to express his appreciation to Professor Daniel Swern of Temple University, Philadelphia, Pa., for his generous help in obtaining all of the nmr spectra.

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(8) (a) The elemental analyses were obtained by Dr. Stephen M. Nagy, Belmont, Mass. (b) Melting and boiling points are uncorrected. The nmr spectra (neat) were recorded on a Varian A-60A spectrometer and the δ values are in parts per million from tetramethylsilane.

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(11) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

Reactions of Chlorine and Iodobenzene Dichloride with Cyclodecenes¹

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Additions to medium-ring olefins have led to data of considerable significance for reaction mechanisms.^{3,4}

(1) (a) Based on the Ph.D. Dissertation of D. B. S., Louisiana State University, 1969. The financial assistance from the Charles E. Coates Memorial Fund, donated by George H. Coates, for preparation of the Ph.D. Dissertation of D. B. S. is gratefully acknowledged. (b) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968, paper number 39.

(2) National Aeronautics and Space Administration Trainee, 1964–1966. (3) For reviews of medium ring chemistry, including some additions to olefins, see (a) V. Prelog and J. G. Traynham, in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 9; (b) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev. (London)*, **20**, 148 (1966).

(4) (a) J. G. Traynham and T. M. Couvillon, *J. Amer. Chem. Soc.*, **89**, 3205 (1967); (b) M. Fisch and G. Ourisson, *Chem. Commun.*, 407 (1965); (c) J. G. Traynham, G. F. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967); (d) J. Sicher, J. Zavada, and M. Svoboda, *Collect. Czech. Chem. Commun.*, **27**, 1927 (1962); (e) M. Havel, M. Svoboda, and J. Sicher, *ibid.*, **34**, 340 (1969). (We acknowledge with gratitude the receipt of a prepublication copy of this paper from Professor Sicher.)

Both vicinal and transannular addition products have been obtained, and transannular processes may dominate the overall reaction.^{3,4} Halogen additions to olefins have received much attention and have been shown to proceed by both cationic and radical pathways,⁵ but few halogen additions to medium-ring cycloalkenes have been reported.

Bromine adds to *cis*-cyclodecene in carbon tetrachloride at –10° to form both *trans*-1,2-dibromocyclodecane (10% yield) and *cis*-1,6-dibromocyclodecane (40% yield), as well as other components in a complex mixture.^{4d,e} Only the transannular product, *trans*-1,6-dibromocyclodecane, has been identified in the product mixture obtained from *trans*-cyclodecene under the same conditions.^{4d} Both bromine⁶ and chlorine^{4a,7} add normally to *cis*-cyclooctene to produce *trans*-1,2-dihalocyclooctanes.

We report here an investigation of the reactions of chlorine and of iodobenzene dichloride,⁸ both under ionic and radical conditions,^{5,8} with the isomeric cyclodecenes. Product-distribution data have been obtained and are summarized in Table I.

The production of a single, vicinal addition product in the reaction of *cis*-cyclodecene with chlorine, under both ionic and radical conditions, contrasts surprisingly with the predominant formation of the transannular addition product when bromine^{4d,e} or iodobenzene dichloride is the reactant. Although we do not yet have enough energy data to have predicted these results with any confidence, the precise course of these halogen additions undoubtedly depends on a delicate balance of energy requirements among competing pathways. The energy requirements for product formation from a 2-chlorocyclodecyl intermediate (cation or radical) and chlorine is lower than that for reaction of the intermediate with iodobenzene dichloride (or bromine) and for transannular hydrogen shift. With iodobenzene dichloride or bromine as reactant, transannular hydrogen shift in the intermediate is favored over direct product formation.⁹

No vicinal dichloride was obtained from *trans*-cyclodecene reacting with either chlorine or iodobenzene dichloride. The greater internal strain in the *trans*-cyclodecene compared with the *cis* isomer may be wholly responsible for the occurrence of transannular hydrogen shifts, but geometry may be an important factor, also. Examination of a Dreiding molecular model of *trans*-cyclodecene indicates that one side of the C=C π cloud is effectively blocked by the chain of methylene groups in the ring, and, without severe conformational change, the initially formed intermediate would not be likely to form vicinal product by *anti* addition. The large amount of 3-chloro-1-cyclodecene formed from *trans*-cyclodecene, compared with that from *cis*-cyclodecene, probably is related in a similar fashion to the conformations of the olefins.

Dechlorination of the *trans*-1,2-dichlorocyclodecane

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