provided by the nmr spectrum (CCl_4). The methyl protons of the isopropyl group afford doublets at δ 0.99 and 1.10 ppm,[7] and the sharp band at δ 9.40 ppm unequivocally shows the presence of a CHO group carrying no α hydrogen. The line at δ 2.25 ppm consisting of four protons is assigned to CH_2 group in the ring. The signal at δ 5.92 and 6.68 ppm (each doublet J = 6 cps) can be assigned to vinyl protons of β and γ positions, respectively.

Compound 2 may be of synthetic interest from the viewpoint of its possessing the possibility of further transformations and it is fascinating that the compound can be obtained quantitatively by a simple procedure.

Experimental Section[8]

Acid Treatment on (−)-Perillaldehyde.—A mixture of (−)-perillaldehyde (10 g) and 10% aqueous sulfuric acid (150 ml) was refluxed for 3 hr at 120–130°; then the resulting solution was extracted with ether. The ether solution was neutralized, washed with water, dried over anhydrous sodium sulfate, and distilled *in vacuo* to give 9 g of 2, bp 81–82° (6 mm), in a 90% yield: d^{20}_4 0.9795; $n^{20}D$ 1.5283, MD 47.18° (calcd 45.06°); ν_{max} 2700, 2800, 1666 (CHO), 1570 ($\alpha\beta,\gamma\delta$-conjugated diene), 1360, 1380 (isopropyl), 780, 840 cm^{-1} (double bond); λ^{MeOH}_{max} 315 mμ (ϵ 15,600); δ 0.99, 1.10 (d, 6 H), 9.40 (s, 1 H), 2.25 (s, 4 H), 5.92, 6.68 ppm (each doublet J = 6 cps, 2 H); semicarbazone mp 193–194°.

Anal. Calcd for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.95; H, 8.49; N, 20.21.

Registry No.—1, 18031-40-8; 2, 1197-15-5; semicarbazone of 2, 18039-53-7; sulfuric acid, 7664-93-9.

Acknowledgments.—The authors are indebted to Dr. Yuzo Inouye, Institute for Chemical Research, Kyoto University, for his kind advice and suggestions. They also wish to express their thanks to Japan Electron Optic Laboratory Co., Ltd., for nmr analysis.

(7) S. K. Paknikar and S. C. Bhattacharyya, *Tetrahedron*, **18**, 1509 (1962).

(8) All melting and boiling points are uncorrected. Microanalysis was performed on a Yanagimoto CHN-corder. Ir spectrum was obtained with a Hitachi EPI-2 spectrophotometer using sodium chloride liquid film cell. Uv spectrum was obtained with a Hitachi EPS-3 recording spectrophotometer in methanol solution. The nmr spectrum has obtained with Japan nuclear magnetic resonance spectrum spectrophotometer JNM-4 H-100 in carbon tetrachloride contained tetramethylsilane (TMS) as an internal reference. Chemical shifts are expressed in δ values (parts per million) from TMS.

Reaction of *gem*-Dibromocyclopropanes with Morpholine

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The reaction of *gem*-dihalocyclopropanes with electrophilic or nucleophilic reagents is a useful method of extending the carbon chain of olefins and leads to several otherwise difficultly accessible molecules.[2] In a previous paper[2] it was shown that a variety of electrophilic reagents readily react with *gem*-dihalocyclopropanes to yield allyl derivatives or dienes. Since no data exists in the literature on the reaction of basic nitrogen compounds with *gem*-dibromocyclopropanes to give N-substitution products, it was of interest to investigate the reaction of morpholine in the above reaction.

The results of this investigation indicate that refluxing a morpholine solution of substituted *gem*-dibromocyclopropane for 1–154 hr yields β-bromoallylmorpholines or the 3-bromo-1,3-diene as described in Tables I and II. The thermal ring opening of the neat *gem*-dibromocyclopropanes yielded in some cases isolable β-bromoallyl bromides or the 3-bromo-1,3-diene.

This ring-opening reaction takes place readily with the more highly alkylated *gem*-dibromocyclopropanes and follows the same order of reactivity observed with electrophilic reagents.[2] In the case of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (VII), 3-bromo-2,4-dimethyl-1,3-pentadiene (VIII) is obtained in 82% yield even in the absence of any solvent by heating to 160–162° for 2.5 hr. The reaction of 1,1-dibromo-2,2-dimethylcyclopropane (I) with morpholine yielded 3-bromo-2-methyl-4-morpholino-2-butene (II), whereas in the absence of morpholine 1,2-dibromo-3-methyl-2-butene (III) was obtained. The thermal ring opening of other neat *gem*-dibromocyclopropanes does not always lead to the isolation of clearly defined products.

Attempts to thermally rearrange the *cis*- and *trans*-butene-2-dibromocarbene adducts in the absence of solvent yielded tars. However, carrying out the same reaction in refluxing morpholine gave an immediate precipitation of morpholine hydrobromide from the *cis* adduct. The *trans* adduct gave a similar precipitation after a longer period of refluxing. Both *cis*- and *trans*-butene-2-dibromocarbene adducts yielded the same isomeric product (V) as shown by analysis using gas–liquid partition chromatography (glpc) and infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy.

Recently[2] it was reported that these same *cis*- and *trans*-dibromocarbene adducts also yield one isomeric product upon reaction with aqueous silver nitrate or silver acetate–acetic acid.

In the case of *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane the transition states obtained by the favored disrotatory process[3-5] can be formulated as shown in Scheme I, p 4539.

In agreement with the above predictions it is found that *cis*-dimethyl isomer reacts faster than the *trans* isomer. This has also been reported to be true for the *cis* and *trans* isomers of 1,1-dichloro-2-methyl-3-ethoxycyclopropane.[6] In the latter case the *cis* and *trans* isomers also undergo a ring-opening reaction in

(1) (a) The Borden Chemical Co., Central Research Laboratory, Philadelphia, Pa. 19124. (b) This research was described in part in the Ph.D. Thesis of S. R. S., The Pennsylvania State University, University Park, Pa. 1960.

(2) S. R. Sandler, *J. Org. Chem.*, **32**, 3876 (1967), and references cited therein.

(3) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

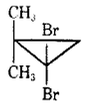
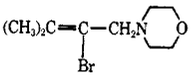
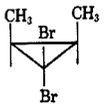
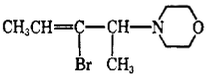
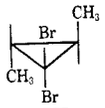
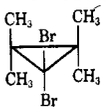
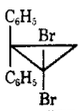
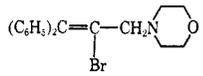
(4) C. H. DePuy, L. G. Schnack, J. W. Hauser, and W. Wiedemann, *ibid.* **87**, 4006 (1965).

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

(6) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

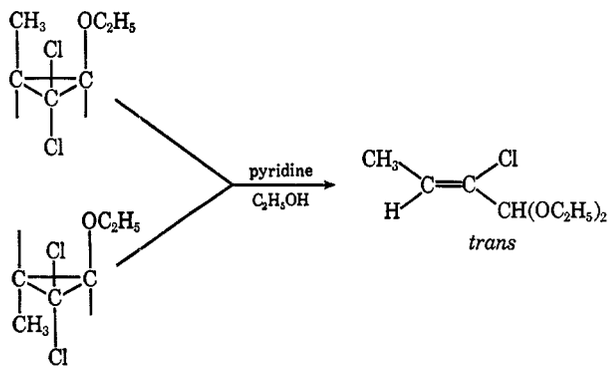
TABLE I

THE THERMAL RING-OPENING REACTION OF SUBSTITUTED *gem*-DIBROMOCYCLOPROPANES IN THE PRESENCE AND ABSENCE OF MORPHOLINE

gem-Dibromocyclopropane, mol	Morpholine, mol	Temp, °C	Time, hr	Product[a]	Yield, %	Bp, °C (mm)	n_D (°C)
 I 0.0527	0.207	128	72	 II	84	110 (5)	1.5121 (23)
I 0.0615	0	195–210	3	$(CH_3)_2C{=}C(Br){-}CH_2Br$ III	60	62–63 (3.5)	1.5471 (21)
 IV 0.0527	0.207	128	24	 V	55	103 (4.0)	1.5113 (20)
IV 0.0527	0	150	3	Tar			
 VI 0.0527	0.207	128	24	V	88	108–110 (5.0)	1.5080 (23)
VI 0.0527	0	150–170	3	Tar			
 VII 0.0277	0.207	128	1	$(CH_3)_2C{=}C(Br){-}C(CH_3){=}CH_2$ VIII	36	46–47 (13.0)	1.4921 (20)
VII 0.100	0	160–162	2.5	VIII	82	47–48 (15.0)	1.4938 (19)
 IX 0.0284	0.207	128	154	 X	78	Mp 90–91	
IX 0.0284	0	150–170	24	Tar			

[a] The glpc analyses of the products were obtained on a 3- and 6-ft column packed with 25% silicone DC200 on Celite at concentration (P) obtained from The Burrell Corp., Pittsburgh, Pa.

the presence of pyridine and ethanol to give the same *trans* product as shown below.



The vinyl proton for *trans*-2-chloro-1,1-diethoxy-2-butene absorbs at δ 6.1 (=CH) which is similar to that observed in compound V (δ 5.78); hence by analogy we assign a *trans* configuration to the methyl group and the carbon bearing the morpholinyl group. The fact that none of the *cis* isomer is produced may be due to either isomerization of the *cis* product during this reaction or to a preferred attack by a nucleophile (morpholine) on carbonium ion (B) to give only the *trans* product. The direction of ring opening using morpholine is identical with that observed with electrophilic reagents[2] and with pyridine–ethanol.[6] Skattebøl found that 1,1-dichloro-2-ethoxy-3,3-dimethylcyclopropane gives a product similar to II on reaction with pyridine–ethanol which has the structure $(CH_3)_2C{=}CCl{-}CH(OC_2H_5)_2$. This compound shows a doublet in the nmr at δ 1.87 [$(CH_3)_2C{=}$] similar to that found for II at 1.83.

The mechanism given above is shown only to illustrate the Woodward–Hoffmann rules[3] and is not

TABLE II

ELEMENTAL AND SPECTRAL ANALYSIS OF PRODUCTS FROM THE THERMAL AND MORPHOLINE INDUCED RING OPENING OF SUBSTITUTED *gem*-DIBROMOCYCLOPROPANES

Compd	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Spectral data[a]
II	46.20	6.85	46.03	6.90	Ir (neat) 6.05 (C=C), 9.0 μ (morpholino group); nmr doublet at δ 1.83 (CH_3C=C), singlet at 3.25 [CH_2—C(Br)=], and the characteristic absorption for the morpholine hydrogens
III	26.45	3.51	26.69	3.54	Ir (neat) 6.07 μ (C=C); nmr doublet at δ 1.83 (CH_3C=C) and a singlet at 4.32 (—CH_2Br)
V[b]	46.20	6.85	46.47	6.96	Ir (neat) 6.03, 11.59 (C=C), 8.98 μ (morpholino group); nmr doublet at δ 1.13 (CH_3CH—N—), doublet at 1.69 (CH_3CH=), quartet at 2.72 (N—CH—CH_3), quartet at 5.98 (CH_3—CH=), and characteristic absorption for the morpholine hydrogen
V[c]	46.20	6.85	46.37	6.99	Same as for compound V
VIII[d]	48.00	6.28	48.02	6.33	Ir (neat) 6.05, 6.12, 11.07, 11.35, 11.75 (C=C), 7.26 μ (CH_2); nmr singlet at δ 1.76 (CH_3C=C), singlet at 1.84 (CH_3C=C), singlet at 4.80 (—CH=C), and singlet at 4.91 (—CH=C)
VIII[e]	48.00	6.28	48.39	6.26	Same as for compound VIII
X	63.80	5.59	63.96	5.73	Ir (KBr) 3.30, 6.26 (C_6H_5), 3.45, 3.50, 3.57 (CH), 6.18, 11.48 (C=C), and 9.0 μ (morpholino group); λ_{max} (CH_3OH) 235 mμ (ϵ_{max} 12,400); nmr singlet at δ 3.25 [=(Br)C—CH_2N] singlet at 7.18 [C_6H_5—C=C(Br)—], and characteristic absorption for the morpholine hydrogens

[a] The integrated spectra were consistent with the assigned structures. [b] Compound V obtained from compound IV. [c] Compound V obtained from compound VI. [d] Compound VIII obtained from VII in the presence of morpholine. [e] Compound VIII obtained from VII in the absence of morpholine.

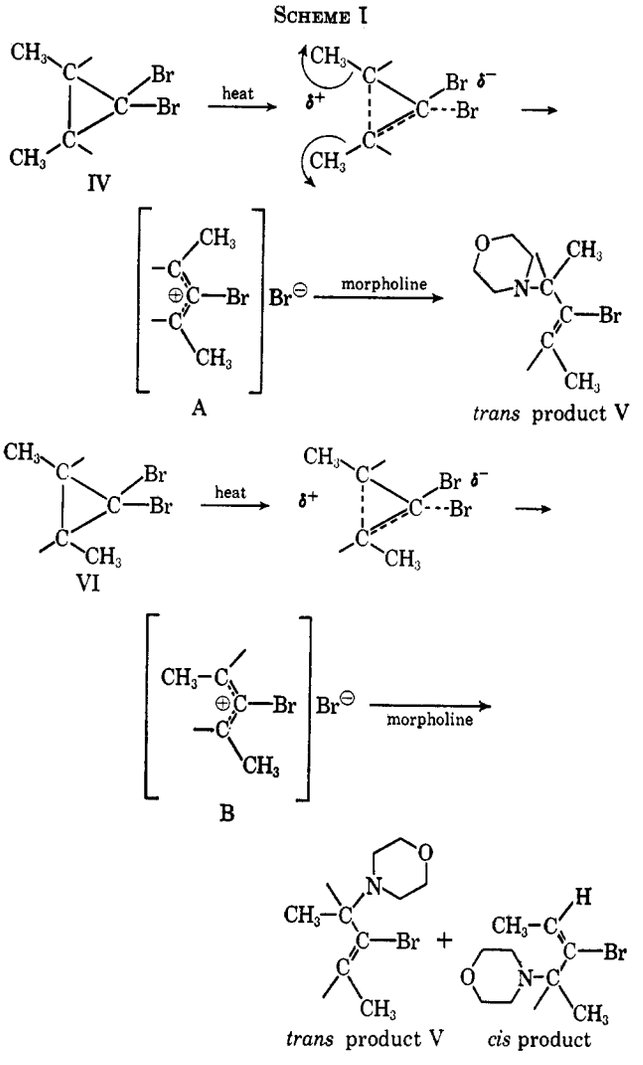
meant to rule out the possibility of product formation through the thermally formed β-bromoallyl bromides. The results shown in Table I with compound I indicates that such a possibility might exist (Scheme II). In addition, it has been reported[7] that the solvolysis in 80% ethanol of 6,6-dibromobicyclo[3.1.0]hexane proceeds simultaneously by its direct reaction with solvent and with the thermally produced 2,3-dibromocyclohexene.

Experimental Section[8]

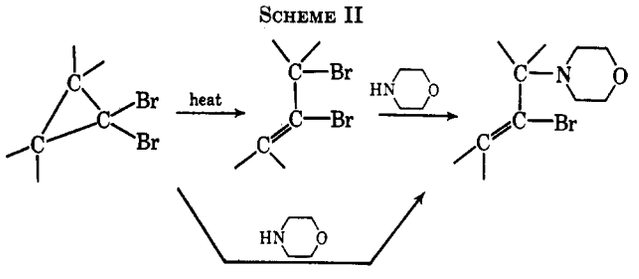
The dibromocarbene adducts were generally prepared by a procedure similar to those described earlier.[9-11] The results of these preparations are presented in a previous paper.[2]

General Procedure for the Thermal Ring-Opening Reaction of Substituted *gem*-Dibromocyclopropanes in the Presence and Absence of Morpholine.—To a single-neck round-bottom flask was added the particular *gem*-dibromocyclopropane with or without morpholine, and the contents were heated under a nitrogen blanket for the specified time. Samples were removed periodically and analyzed by glpc to determine the extent of reaction. Where morpholine was used, the samples were acidified and extracted with ether, dried, concentrated, and distilled under reduced pressure to obtain the product. The experimental conditions and products are described in more detail in Tables I and II.

SCHEME I



SCHEME II



Registry No.—Morpholine, 110-91-8; II, 17853-41-7; III, 17853-42-8; V, 17853-43-9; VIII, 4773-87-9; X, 17853-44-0.

Acknowledgment.—The author wishes to express his appreciation to Professor P. S. Skell of The Pennsylvania State University for his generous help throughout this investigation; to Mr. O. Lauver of the Pennsylvania State University and to Professor D. Swern of Temple University for obtaining the nmr spectra.

(7) L. Gatlin, R. E. Glick, and P. S. Skell, *Tetrahedron*, **21**, 1315 (1965).

(8) (a) The elemental analyses were obtained by Dr. Stephen M. Nagy, Belmont, Mass. (b) Melting and boiling points are uncorrected. The nmr spectra (in CCl_4) were recorded on a Varian Associates A-60-A spectrometer and the δ values are in parts per million from tetramethylsilane. The ultraviolet spectra were obtained on a Beckman DK-1 recording spectrophotometer.

(9) W. von E. Doering and A. K. Hoffman, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

(10) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

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