Samples of the ketone I have been reduced by lithium aluminum hydride in tetrahydrofuran and in an ether–benzene mixture. The reaction product in each case was a viscous oil, which could not be crystallized. Attempts to convert the crude reduction product into a *p*-toluenesulfonyl derivative also were unsuccessful.

3-Triphenylsilylpropylbromide.—A mixture of 10 g. (0.0314 mole) of 3-triphenylsilylpropanol-1 and 5.4 g. (0.02 mole) of phosphorus tribromide was placed in a Schlenk tube and heated for 12 hr. on a steam-bath. Benzene was then added and the mixture hydrolyzed with cold water. After washing the organic layer several times with water, dilute ammonium hydroxide and dilute sulfuric acid, it was filtered and the solvent removed. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. The product, eluted with the same solvent, was recrystallized from ethanol to give 6.8 g. (57%) of 3-triphenylsilylpropyl bromide, m.p. 92–93°.

Anal. Calcd. for $C_{21}H_{21}BrSi$: Si, 7.36. Found: Si, 7.24, 7.36.

4-Triphenylsilylbutyric Acid. (A) From 4-Triphenylsilylbutanol-1.—To a stirred solution of 4-triphenylsilylbutanol-1[11] in 75 ml. of glacial acetic acid, 5 g. (0.05 mole) of chromic acid was added in small portions at 30–32°. The resulting mixture was stirred for 3 hours at 45–46° and subsequently worked up in the same manner as described for 3-triphenylsilylpropionic acid. There was obtained 5.0 g. (73.5%) of 4-triphenylsilylbutyric acid, m.p. 165–167°. Several recrystallizations from a mixture of ethyl acetate and petroleum ether (b.p. 60–70°) raised the melting point to 171–172°.

Anal. Calcd. for $C_{22}H_{22}O_2Si$: Si, 8.09; neut. equiv., 346.4. Found: Si, 8.07, 8.24; neut. equiv., 354.1.

(B) From 3-Triphenylsilylpropyl Bromide.—A Grignard reagent was prepared from 1.3 g. (0.0036 mole) of triphenylsilylpropyl bromide and 0.1 g. of magnesium in 50 ml. of ether. The mixture was carbonated with Dry Ice. The work up in the usual manner yielded 0.1 g. of crude acid. Two recrystallizations from a mixture of ethyl acetate and petroleum ether (b.p. 60–70°) gave needles melting at 172–173°. A mixture melting point with the product prepared by method A was undepressed.

2:3-Benzo-1,1-diphenyl-1-silacyclohepten-2-one-4 (II).—A mixture of 1.5 g. (0.0045 mole) of 4-triphenylsilylbutyric acid and 10 ml. of thionyl chloride was refluxed gently for one hour. Excess thionyl chloride was removed under reduced pressure, the last traces of the reagent by co-distillation with two 10-ml. portions of benzene. The crude acid chloride was dissolved in 15 ml. of nitrobenzene and, with cooling in an ice-bath, 0.60 g. (0.045 mole) of aluminum chloride was added. The mixture was stirred for 30 minutes at room temperature, subsequently hydrolyzed and worked up as described before. On chromatography with alumina, the benzene eluate yielded a small quantity of a viscous oil, which crystallized on treatment with methanol. There was obtained 0.25 g. (17.8%) of ketone II, m.p. 103–105°. Recrystallization from a mixture of methanol and ether raised the melting point of the product to 105–106°.

Anal. Calcd. for $C_{22}H_{20}OSi$: C, 80.42; H, 6.14. Found: C, 80.20, 80.13; H, 6.30, 6.26.

The ketone II gave a semicarbazone, m.p. 177–178°.

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF RHODE ISLAND, KINGSTON, R. I.]

The Free Radical Addition of Hydrogen Bromide to the 1-Bromocycloalkenes[1]

BY PAUL I. ABELL AND CHERRY CHIAO

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The addition of hydrogen bromide to 1-bromocyclobutene, 1-bromocyclopentene and 1-bromocycloheptene under free radical conditions gives ratios of *cis* to *trans* isomers of the 1,2-dibromocycloalkanes of 79:21, 94:6 and 91:9, respectively. These isomers have been separated and characterized. An explanation of the variation in isomer ratios is given in terms of a balance between a mechanistic preference for a *trans* addition process and a steric inhibition to the formation of the *cis* isomers.

Introduction

A tendency toward a *trans* mechanism in the free radical addition of hydrogen bromide to olefins has been observed in a substantial and growing number of cases. Among these are the additions to 1-bromocyclohexene,[2] 1-methylcyclohexene,[2] 1-methylcyclopentene,[3] 1-methylcycloheptene,[4] 1-chlorocyclohexene,[5] *cis*- and *trans*-2-bromo-2-butene,[6] propyne[7] and (using deuterium bromide) *cis*- and *trans*-2-butene.[8] Many of these tests for a stereospecific mechanism have been carried out on cyclic olefins in order to avoid the complications of *cis-trans* isomerization prior to addition. However, the reaction has shown a high degree of stereospecificity in all of the compounds investigated with the exception of 2-bromo-2-norbornene, where the bridged ring structure introduces major steric complications.[9] Of the olefins studied, only 1-bromocyclohexene has been demonstrated to show an almost completely stereospecific path in the addition, yielding *cis*-1,2-dibromocyclohexane contaminated with only 0.3% of the *trans* isomer.[5] It appeared likely to us that this reaction constitutes a special case in that the cyclohexane ring is unique among the simple ring systems in the arrangement of its bonds in axial and equatorial types. Although the steric and mechanistic dif-

(1) A portion of this work was performed under Contract No. DA-19-020-ORD-3171, OOR project 1037 of the Office of Ordnance Research, U. S. Army. Support is gratefully acknowledged. That portion of this paper pertaining to the cycloheptyl compounds is taken from the M. S. thesis of Cherry Chiao, University of Rhode Island, 1958.

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(3) King Howe, Ph. D. thesis, University of Wisconsin, 1957.

(4) Bruce Bohm, M. S. thesis, University of Rhode Island, 1958.

(5) H. L. Goering and L. L. Sims, THIS JOURNAL, **77**, 3465 (1955).

(6) H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957).

(7) P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

(8) P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

(9) N. A. LeBel, Abstracts of Papers of American Chemical Society Meeting, Boston, Mass., April, 1959, p. 4-O.

ferences in these two types of bonds have been demonstrated largely with ionic reactions, it has been pointed out[10] that they should also play an important role in the stereochemistry of free radical reactions. Accordingly, it was decided to investigate the stereochemistry of the free radical addition of hydrogen bromide to 1-bromocyclobutene, 1-bromocyclopentene and 1-bromocycloheptene, which would complete the series of smaller rings. A correlation of ring size with stereospecificity might yield data by which the stereochemistry could be clarified. We were especially interested in the reaction with 1-bromocyclobutene, since the reaction would provide a test of the ability of the intermediate cyclobutyl free radical to retain the strained ring structure without rearrangement. Finally, an opportunity would be offered to prepare these cyclic vinyl bromides and to examine their properties and also those of the resulting dibromocycloalkanes.

Results

The 1-bromocycloalkenes, synthesized by known methods (see Experimental section), were dissolved in pentane, subjected to ultraviolet illumination and dry hydrogen bromide was passed through the solution at 0–5°. The products, isolated by evaporation of the pentane, were mixtures of the *cis*- and *trans*-1,2-dibromocycloalkanes, in which the *cis* isomer predominated. The products of ionic addition, the 1,1-dibromocycloalkanes, were not found in any of these reactions. The reaction products were analyzed by infrared spectroscopy or by gas chromatography. The results are summarized in Table I. Several runs for each olefin are given to illustrate the spread of the data.

TABLE I

ISOMER DISTRIBUTION AND YIELDS IN THE HBr ADDITION TO 1-BROMOCYCLOALKENES

Olefin, 1-bromo-	Run[a]	Yield, satd. products	Mole % *cis* isomer	Analytical method[b]
Cyclobutene	1	85.7	76	GC
Cyclobutene	4	90.7	80	GC
Cyclobutene	5	...	78	GC
Cyclobutene	6	...	82	GC
Cyclopentene	1a	96.2	94	GC, IR
Cyclopentene	2a	98.9	91	GC, IR
Cyclopentene	7a	92.6	95	GC, IR
Cycloheptene	2b	83.5	90	IR
Cycloheptene	3b	84.5	92	IR

[a] Runs selected are free radical runs in which experimental difficulties were absent. [b] GC refers to gas chromatography IR to infrared spectrophotometery.

All of the products were shown to be stable toward reaction conditions by exposure to hydrogen bromide and ultraviolet illumination in pentane, and are therefore presumed to be initial products.

The structures of the *cis*-1,2-dibromocycloalkanes were established by a variety of techniques. Purified samples of the *cis* isomers were found to give correct elemental analyses, and, by measurement of densities and refractive indices, the molar refractivities were calculated and shown to be in good agreement with those obtained by addition of structural increments. These *cis* isomers were shown to differ in their physical properties from the 1,1-dibromocycloalkanes. They eliminated hydrogen bromide in base to give the starting vinyl halides. Additional effort in the case of *cis*-1,2-dibromocyclobutane showed that the infrared spectrum of this compound was consistent with a cyclobutane ring, that the compound was saturated toward bromine in carbon tetrachloride, that the molecular weight was in agreement with the formula and that the nuclear magnetic resonance spectrum was consistent with the assigned structure.

Discussion

The observed stereochemistry of the free radical addition of hydrogen bromide to olefins can be explained mechanistically in two different ways, as was emphasized recently by Goering.[11] The first explanation is that the lifetime of the "classical" intermediate free radical (path 1, Fig. 1) is so short that changes in conformation do not take place prior to the chain transfer step which takes place from the less hindered side.

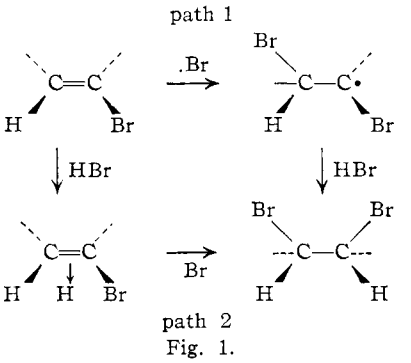

Fig. 1.

The second explanation, one tested for unsuccessfully by Goering,[5] but certainly not yet excluded as a possibility, involves the formation of a π-complex between hydrogen bromide and the olefin. This complex collapses stereospecifically as the bromine atom attacks the π-electrons[12–14] from the opposite side (path 2, Fig. 1). The collapse of the π-complex is necessarily highly stereospecific, and for this reason fails to explain the varying degrees of stereospecificity observed in the present paper. Thus, the first explanation (path 1, Fig. 1) appears preferable, since it allows for an approach of the hydrogen bromide from either side of the free radical carbon in the chain transfer step, but with a substantial preference for the less hindered side. The variation of specificity with ring size is thus attributable to the availability of unhindered approach to the free radical carbon coupled with a degree of reluctance to force the bromines into a *cis* configuration. Accordingly, the variation in *cis-trans* isomer formation observed in the present work can be explained by these terms, in line with

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(11) H. L. Goering, *Angew. Chem.*, **70**, 479 (1958).

(12) R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945).

(13) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. 1, Princeton Univ. Press, Princeton, N. J., 1958, p. 68.

(14) This is in contrast to the back-side attack on the σ-bond as proposed by A. R. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, THIS JOURNAL, **79**, 5621 (1957).

the classical free radical intermediate. The cyclobutane ring is quite rigid in its bond angles, and forcing the two bromine atoms into a true, unskewed *cis* configuration may be expected to be difficult. The cyclopentane ring has some flexibility,[15] and a *cis* configuration of the bromines, while crowded, is relieved by puckering of the ring. Thus, the 1-bromocyclobutene adduct shows the least stereospecificity and the 1-bromocyclopentene adduct a somewhat greater specificity (Table I). Only in the six-membered ring is the *cis* relationship one in which crowding of the two bromine atoms is negligible, and therefore the only ring size investigated producing exclusively the *cis* isomer. In the cycloheptane ring the interpretation is more difficult owing to the partially fixed, partially flexible nature of this ring. Models of the intermediate free radical indicate that there is some of the same axial–equatorial bond character as with the six-membered ring, but that the "extra"carbon in the ring produces a flexibility that, in some conformations, allows a substantial interaction of the two bromines. However, the radical can assume several conformations, including the one in which the recently added bromine has not moved from an initial axial conformation, which will lead to the *cis*-dibromide by approach of the hydrogen bromide from the least hindered side in the hydrogen abstraction step. As a consequence the seven-membered ring yields some of the *trans*-dibromide, although the *cis* isomer predominates.

This view of the "classical" mechanism (path 1, Fig. 1) is supported by the work of LeBel[9] on 2-bromo-2-norbornene. A π-complex intermediate would be expected to collapse stereospecifically into either *endo-cis*- or *exo-cis*-2,3-dibromonorbornane, while a classical intermediate, having the approach of the hydrogen bromide hindered by the methylene bridge (*exo* side), the dimethylene bridge (*endo* side) and the 3-bromine atom (probably *exo*), would be expected to yield products representing a balance among these steric repulsions. The actual products, 5/7 *trans*-2,3-dibromonorbornane and 2/7 *exo-cis*-2,3-dibromonorbornane, indicate a preference for the *exo* approach (Fig. 2).

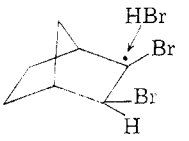

Fig. 2.

Among the more intriguing phases of this investigation was the reaction of hydrogen bromide with 1-bromocyclobutene. It has been demonstrated[16] that cyclobutane shows a greater resistance toward becoming a free radical than do either cyclopentane or cyclohexane, as indicated by hydrogen abstraction studies, and possibly the same conclusion can be reached from the work of Hart and Wyman[17] on the decomposition of cycloalkylformyl peroxides. While it did not appear likely that a cyclobutyl free radical would be so unstable as to refuse to add hydrogen bromide at all or to rearrange to a ring-opened product, in view of the notable reluctance of free radicals to rearrange[18], it appeared worthwhile to examine the possibility. Our results show that the products of the hydrogen bromide addition still retain the cyclobutyl ring, and it is evident that the ring is stable under the reaction conditions.

(15) K. S. Pitzer and W. E. Donath, THIS JOURNAL, **81**, 3213 (1959).

(16) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(17) H. Hart and D. P. Wyman, THIS JOURNAL, **81**, 4891 (1959)

Experimental[19]

1-Bromocyclobutene was prepared according to published procedures with the modifications noted herein. Diethyl α,α'-dibromoadipate, prepared according to the method of Ingold,[20] was cyclized with sodium cyanide in alcohol to 1,2-dicarbethoxy-1-cyanocyclobutane. The *meso* isomer was not separated, but the crude esters were dried and used directly in the next step. The cyanoester was hydrolyzed to 1,1,2-cyclobutanetricarboxylic acid with barium hydroxide and after isolation of the acid it was decarboxylated by heating.[21] The 1,2-cyclobutanedicarboxylic acid was conveniently isolated by continuous ether extraction. It was found expedient to isomerize the mixed isomers of the *cis*- and *trans*-1,2-dicarboxylic acids to the pure *trans* isomer using aqueous hydrochloric acid at 190° in a stainless steel bomb[22] to assist in the purification of the acid and thus improve the yields in the subsequent steps. The *trans*-acid, converted to the silver salt, was subjected to the Hunsdiecker reaction.[23] Finally the resulting *trans*-1,2-dibromocyclobutane was purified by repeated freezing at 0° with removal of material that did not crystallize; m.p. 4.0–5.0°, lit.[24] m.p. 4.7–5.7°. It was converted to 1-bromocyclobutene by treatment with powdered potassium hydroxide at 110°[25] in yields of up to 85%, b.p. 92.5–93° (756 mm.), n^{25}D 1.4531, lit.[25] b.p. 92.5–93.5°.

1-Bromocyclopentene.—Dehydrohalogenation of *trans*-1,2-dibromocyclopentane with molten potassium hydroxide at 150° gave the vinyl halide in yields, after fractional distillation, of up to 20%, b.p. 128.5° (760 mm.), n^{25}D 1.4999.

Anal. Calcd. for C_4H_5Br: C, 40.84; H, 4.80. Found: C, 40.94; H, 4.75.

1-Bromocycloheptene.—Cycloheptanone was reduced with lithium aluminum hydride in ether and the resulting alcohol acetylated with acetic anhydride. The cycloheptyl acetate was pyrolyzed to cycloheptene at 490–500° in a glass column packed with short pieces of Pyrex glass tubing, in yields of 85%. Bromination of the cycloheptene gave *trans*-1,2-dibromocycloheptane, which then was converted to 1-bromocycloheptene using the method of Kohler, Tishler, Potter and Thompson,[26] but using trimethylamine rather than dimethylamine as the dehydrohalogenating agent; yield 12%, b.p. 87.3° (31 mm.), n^{25}D 1.5150.

All three of the above 1-bromocycloalkenes were shown to be homogeneous by gas chromatography. Their vinyl halide character was demonstrated by their failure to react with hot alcoholic silver nitrate solution.

Addition of Hydrogen Bromide.—The free radical addition reactions were carried out in purified pentane using anhydrous hydrogen bromide. The reactions were run in a quartz flask, partially submerged in ice-water, and illuminated at a distance of about one inch, using an ultraviolet irradiation source consisting of a Hanovia type 30600 quartz mercury-arc lamp. The flask was fitted with a sintered glass bubbler tube and a condenser protected from moisture with a calcium chloride drying tube. The reactions were usually run on a scale of about 2 g. of vinyl halide in 100 ml. of pentane. The reactions were complete in an hour and crude yields of products running to about 90% (Table I) were obtained by careful evaporation of the pentane.

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(19) Melting points are uncorrected. Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(20) C. K. Ingold, *J. Chem. Soc.*, **119**, 951 (1921).

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TABLE II

PHYSICAL CONSTANTS OF *cis* AND *trans*-1,2-DIBROMOCYCLOALKANES

Ring size	Isomer	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{25}D$	d^{25}	MR Found	MR Calcd.
4	*cis*	196.4	755	−13	1.5478	1.995	34.06	34.00
	trans	174.6	755	4.0–5.0	1 5333	1 923	34.55	34 C0
5	*cis*	91.0–93.0	13	−11	1 5483	1.872	38.70	38 62
	trans	72.4–72 6	15	−12 5	1.5460	1 857	38.88	38.62
6[a]	*cis*	103.8–104.1	9	10 0–10.5	1.5523	1.804	42.89	43.24
	trans	90.1–92.3	9	−4.5	1.5507	1.784	43 27	43 24
7	*cis*	96.0–98.3	2	6.0–6.4	1.5526	1.731	47.31	47.86
	trans	82 8–83.0	1.9	9.0–9.5	1.5530	1.725	47 49	47.86

[a] All data for these two isomers taken from ref. 5.

Analysis of the Products.—The crude products were examined by gas chromatography (with the exception of the cycloheptyl compounds, which decomposed before vaporizing) using a Perkin–Elmer type C column (silicone oil DC-200) 2 meters long. The *cis* and *trans* isomers of the 1,2-dibromocycloalkanes were readily differentiated. Quantitative analysis was carried out with area calibrations obtained with pure *cis* and *trans* isomers. The dibromocycloheptane products were analyzed by infrared spectrophotometry. The *cis* isomer had absorption bands at 9.48 and 12.34 μ, while the *trans* isomer had a band at 12.10 μ, all free of interference.

It was necessary to have comparison samples of the 1,2-dibromocycloalkanes of very high purity. The *trans* isomers were obtained readily by careful fractionation of the *trans*-dibromides used in the preparation of the vinyl halides, both by distillation and by recrystallization. The *cis* isomers were available only through the addition reaction itself. With the five- and seven-membered rings a fractional crystallization of the crude addition product of hydrogen bromide to the 1-bromocycloalkene produced the *cis*-dibromides in the pure state. The large amount of *trans* dibromide formed in the addition to 1-bromocyclobutene made this route impossible, but a satisfactory sample was obtained using a 3-meter preparative gas chromatography column of type C. All of these isomers were shown to be free of impurities by gas chromatography, except that the seven-membered ring dibromides were judged pure by the absence of characteristic absorption bands of other isomeric dibromides in their infrared spectra. All of these dibromides were checked for stability under reaction conditions. In no instance was there evidence for any interconversions between *cis* and *trans* isomers. The physical constants of these dibromides are given in Table II.

Anal. (*cis*-1,2-dibromocycloalkanes). Calcd. for $C_4H_6Br_2$: C, 22.46; H, 2.83; Br, 74.74. Found: C, 22.47; H, 2.74; Br, 74.77. Calcd. for $C_5H_8Br_2$: C, 26.35; H, 3.54. Found: C, 26.53; H, 3.62. Calcd. for $C_7H_{12}Br_2$: C, 33.02; H, 4.68. Found: C, 32.84; H, 4.73.

1,1-Dibromocyclobutane.—The preparation of 1,1-dibromocyclobutane by the method of Willstätter and Bruce[27] did not give a homogeneous product, despite a constant boiling point of 160°, but was contaminated by about 15% of *trans*-1,2-dibromocyclobutane, as demonstrated by gas chromatography. However, the principal product had a retention time much shorter than either the *cis*- or the *trans*-1,2-dibromocyclobutane and did not show up in any of the free radical reactions.

1,1-Dibromocyclopentane was prepared in the same manner[27] as above, using anhydrous hydrogen bromide in glacial acetic acid to effect ionic addition to 1-bromocyclopentene. The product distilled at 182°, but was not completely homogeneous to gas chromatography. Its boiling point and retention time clearly differentiated it from the 1,2-dibromocyclopentane isomers, however. No evidence for this compound was found in the radical addition reactions.

1,1-Dibromocycloheptane.—The ionic addition of hydrogen bromide to 1-bromocycloheptene in ether with added diphenylamine and ferric chloride gave a homogeneous product, 1,1-dibromocycloheptane, b.p. 96.0-98.3° (8 mm.), $n^{20}D$ 1.5458, m.p. −5.3–4.5°, yield 60%. The infrared spectrum was quite different from those of the *cis* and *trans* isomers of 1,2-dibromocycloheptane. Hydrolysis of this *gem*-dibromide produced a ketone, identified as cycloheptanone by its 2,4-dinitrophenylhydrazone. There was no evidence in the infrared spectra of the free radical addition products for the presence of this compound.

Added Evidence for the Structure of *cis*-1,2-Dibromocyclobutane.—Samples of this *cis*-dibromide were separated and purified by gas chromatography. These samples were shown to be saturated to bromine in carbon tetrachloride. A molecular weight determination by freezing point depression in benzene confirmed a $C_4H_6Br_2$ formula (calcd. mol. wt. 214, found mol. wt. 217). The infrared spectrum of the purified *cis* isomer showed the characteristically shortened wave lengths for the carbon–hydrogen stretching mode of vibration as demonstrated by Roberts and Chambers[28] for cyclobutyl chloride and cyclobutyl bromide. These investigators observed absorption at 3.37 and 3.34 μ for the bromide and chloride, respectively. Absorption at 3.34 and 3.38 μ was observed by us for both the *cis* and the *trans* isomers of 1,2-dibromocyclobutane. A nuclear magnetic resonance spectrum[29] of the *cis* isomer of 1,2-dibromocyclobutane showed a complex band, possibly a quintet, at 282 c.p.s. relative to tetramethylsilane as an internal standard, and a similar band at 268 c.p.s. was observed in the spectrum of the *trans* isomer. These spectra were run in carbon tetrachloride solution at 60 mc. The *cis* isomer also showed a triplet centered at 156 c.p.s., while the *trans* isomer gave a broad and very complex band centered at 153 c.p.s. These latter have about twice the area of the bands mentioned first and are therefore assigned to the methylene hydrogens. The similarity of the spectra suggests *cis-trans* isomers, but the rigid geometry of the ring creates spin couplings and second-order effects difficult to interpret. Finally, dehydrohalogenation of the mixed isomers obtained from a free radical addition reaction, 2.00 g., by refluxing with alcoholic potassium hydroxide for 1.5 hr., gave a product, which by gas chromatography was shown to be a mixture of about 4/5 1-bromocyclobutene and 1/5 *trans*-1,2-dibromocyclobutane; yield 1.20 g., 86%.

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(28) J. D. Roberts and U. C. Chambers, THIS JOURNAL, **73**, 5030 (1951).

(29) Kindly furnished by Varian Associates, Palo Alto, Calif.