Reaction of 1-Bromomethylene-2,2-dimethylcyclobutane with Potassium *tert*-Butoxide

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Received August 19, 1970

An equimolar mixture of *trans*- and *cis*-1-bromomethylene-2,2-dimethylcyclobutane (**1a** and **1b**) rearranges with potassium *tert*-butoxide to a 2.2:1 mixture of 1-bromo-3,3-dimethylcyclopentene (**2a**) and 2-bromo-3,3-dimethylcyclopentene (**2b**). Pure *trans*-1-bromomethylene-2,2-dimethylcyclobutane (**1a**) gives a 16:1 ratio of the same products. Isomerization of **1a** and **1b** occurs under the reaction conditions, isomer **1a** being favored. These results are interpreted in terms of a cleavage–recombination mechanism (Scheme IV) for the base-catalyzed ring-enlargement reaction of halomethylenecyclobutanes.

In the preceding paper[1] the base-induced rearrangement of halomethylenecyclobutanes to the corresponding ring-enlarged products was discussed (eq 1).

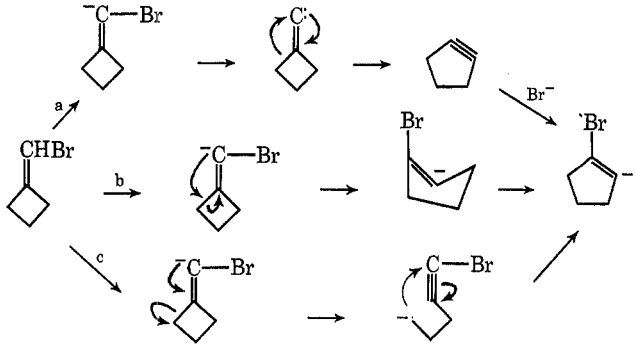
(1)

In an effort to learn more about the mechanism of this unusual type of transformation, an unsymmetrically substituted methylenecyclobutane, 1-bromomethylene-2,2-dimethylcyclobutane (**1**), has been synthesized and subjected to the reaction conditions. The results of this study, reported herein, provide some insight into the nature of this rearrangement reaction.

Results and Discussion

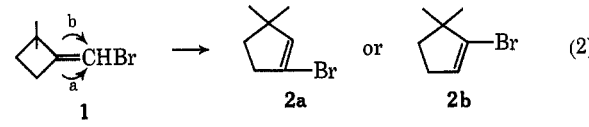
We have previously considered three basic mechanisms for the conversion of bromomethylenecyclobutane to 1-bromocyclopentene.[2] These mechanisms are outlined in Scheme I. Each has its own inherent

SCHEME I



defects. Thus, mechanism a, the carbene–cyclopentyne route, is quite unlikely considering the trapping studies discussed previously.[1] Mechanism b involves a front-side carbanionic rearrangement analogous to the Wittig and Stevens rearrangements (recent evidence actually suggests these are ion-radical processes[3]), but here a *trans*-cyclopentene anion would be involved as the immediate product. Mechanism c, cleavage–recombination, is perhaps the most attractive of the three mechanisms suggested, but it necessitates cyclobutyl ring opening to an unstabilized anion, an unexpected process.[4] Moreover, one might anticipate the isolation of acyclic products from the reaction, and such has not been the case to date.

To decide among these three mechanisms or some alternate possibility for the base-catalyzed ring-enlargement reaction of halomethylenecyclobutanes, an unsymmetrically substituted bromomethylenecyclobutane derivative, 1-bromomethylene-2,2-dimethylcyclobutane (**1**), was studied. With compound **1** there are two possible modes of ring enlargement (eq 2): route a,



1 **2a** **2b** (2)

where the less substituted carbon migrates leading to 1-bromo-3,3-dimethylcyclopentene (**2a**), or route b, where the more highly substituted carbon migrates leading to 2-bromo-3,3-dimethylcyclopentene (**2b**). Another aspect of this system which must be considered is its stereochemistry. Compound **1** can exist in two geometric forms, the trans isomer **1a** and the cis isomer **1b**. Our plan was to synthesize the two isomers and

1a **1b**

subject each to the reaction conditions to determine whether there was a preference for the production of **2a** or **2b**.

The starting point for the synthesis of isomers **1a** and **1b** was 2,2-dimethylcyclobutanone which was prepared by the method of Agosta and Herron[5] with some modifications (see Experimental Section). The planned syntheses of the two isomers are outlined in Scheme II. Neither route was totally successful. As with cyclobutanone itself,[1] the Wittig reaction with 2,2-dimethylcyclobutanone and the bromomethylene ylide[6] gave large amounts of recovered ketone and no bromomethylene compound under a variety of conditions, and this direct route to the trans isomer **1a** had to be abandoned. Interestingly, the planned route to the cis isomer **1b** led ultimately to the trans isomer **1a** instead.

(1) K. L. Erickson, J. Markstein, and K. Kim, *J. Org. Chem.*, **36**, 1024 (1971).

(2) K. L. Erickson, B. E. Vanderwaart, and J. Wolinsky, *Chem. Commun.*, 1031 (1968).

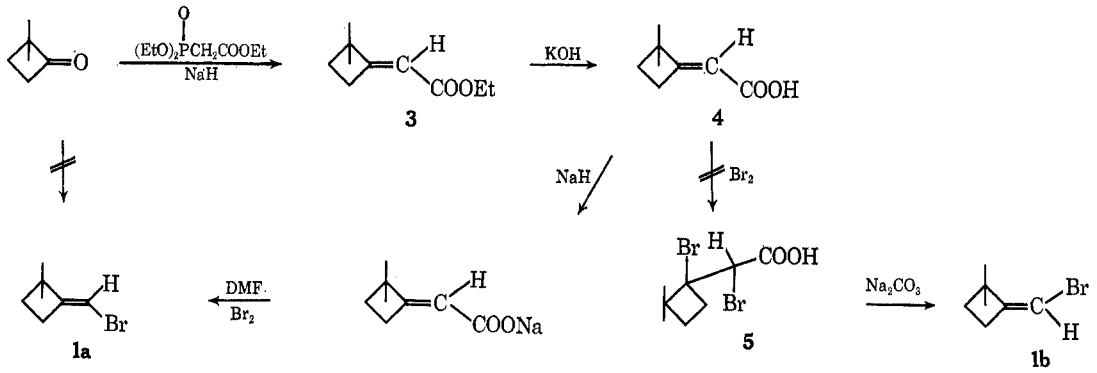
(3) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *ibid.*, 576 (1970); G. F. Hennion and M. J. Shoemaker, *J. Amer. Chem. Soc.*, **92**, 1769 (1970); R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226 (1969); U. Schoellkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 2315 (1969).

(4) R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 288.

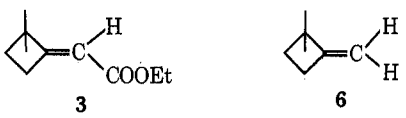
(5) W. C. Agosta and D. K. Herron, *J. Org. Chem.*, **34**, 2782 (1969).

(6) G. Koebrich, *Angew. Chem. Int. Ed. Engl.*, **1**, 51 (1962); G. Koebrich, H. Trapp, K. Flory, and W. Drischel, *Ber.*, **99**, 689 (1966).

SCHEME II



Unsaturated ester **3** was formed in 90% yield from the ketone. As expected,[7] no more than trace quantities of the cis isomer were formed. The assignment of stereochemistry to compound **3** is based upon a comparison of its nmr spectrum with that of 2,2-dimethyl-1-methylenecyclobutane (**6**). The *gem*-dimethyl group



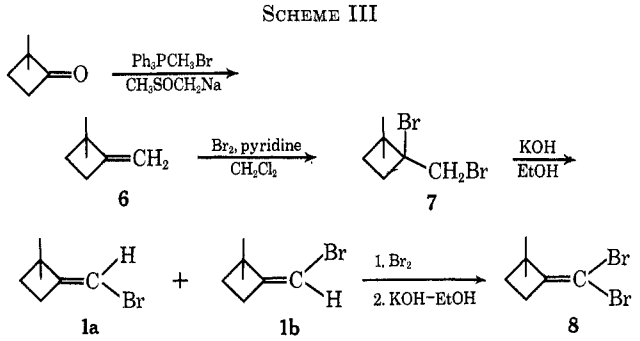
appears at δ 1.24 in the hydrocarbon and at δ 1.25 in the ester. If the ester group were cis to the *gem*-dimethyl group, one would expect the position of the methyl absorption to be substantially different from that in **6**. Moreover, the allylic methylene group absorbs at δ 3.07 in **3** and at δ 2.60 in **6**, the downfield shift in **3** being expected if the ester group is cis to the allylic protons as indicated.

Hydrolysis of ester **3** proceeded in high yield to the unsaturated acid **4** whose nmr spectrum showed that the trans stereochemistry had been retained. Thus, the *gem*-dimethyl group appeared at δ 1.25 and the allylic methylene group at δ 3.08. All attempts to cleanly convert this acid to the dibromo acid **5** failed, however. A variety of brominating agents were used together with an even wider variety of conditions. In each case mixtures of products were obtained whose spectral data indicated lactones and unsaturated bromo acids. These materials were not identified, but it is likely, due to the sluggish uptake of bromine at the electron-poor double bond, that allylic bromination and/or isomerization of the double bond is occurring with subsequent bromination, dehydrobromination, etc. Hydrogen bromide was produced in all of these reactions.

Earlier work with other ring systems that behaved similarly had led to an alternate method of producing the desired exocyclic vinyl bromide from the unsaturated acid.[8] This method involves preparation of the dry sodium salt of the unsaturated acid followed by bromination in anhydrous DMF. When this method was applied to acid **5**, the *trans*-vinyl bromide **1a** was produced in low yield. The stereochemistry of **1a** was again assigned on the basis of its nmr spectrum. The *gem*-dimethyl group appeared at δ 1.23 compared to δ 1.24 in **6** and δ 1.25 in **3** and **4**, strongly suggesting that the bromine is trans to the methyls. However, the position of the allylic methylene group (δ 2.58) was not markedly different from that in compound **6** (δ 2.60). Confirmation that the assignment was correct came when the other isomer **1b** became available (*vide infra*). The production of the trans isomer **1a** in this bromination was predicted on the basis of earlier work with *cis*- and *trans*-stilbene carboxylates and *cis*- and *trans*-cinnamates.[9]

With one isomer in hand, a route was sought to produce the other. Scheme III shows the method used

SCHEME III



which led to an equimolar mixture of cis and trans isomers. The conversion of 2,2-dimethylcyclobutanone into **6** proceeded well, and without purification this material was brominated in the usual fashion for terminal olefins.[8] Dehydrobromination of **7** gave roughly 1:1 mixtures of **1a** and **1b**. These isomers could not be resolved on a variety of vpc columns, but nmr clearly established the presence of both isomers as well as the ratio of each. While the *gem*-dimethyl group in **1a** appeared at δ 1.23, that of **1b** came at δ 1.34. The downfield shift of these methyl protons is expected for the isomer where the bromine is cis and supports the earlier assignment of the trans isomer. The position of the allylic and nonallylic methylene groups were identical in both isomers, but the olefinic protons differed, δ 5.62 in the cis isomer and δ 5.77 in the trans. The ratio of trans to cis could be obtained by measuring the ratio of the methyl signals or the ratio of the vinyl hydrogen signals.

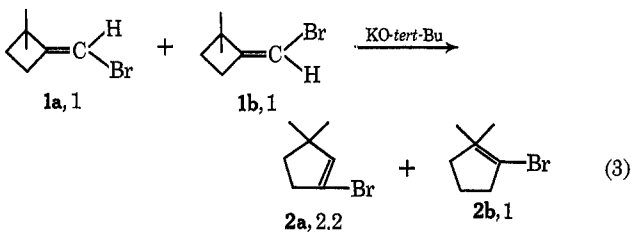
To provide further evidence for the correct assignment of stereochemistry to isomers **1a** and **1b**, dibromomethylenecyclobutane (**8**) was synthesized (Scheme III). The methyl hydrogens of **8** should absorb at the same position in the nmr as those of **1b** if the latter is the cis isomer. In fact, the nmr spectrum of **8** was

(7) A. Maercker, *Org. Reactions*, **14**, 313 (1965).
(8) J. Wolinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).
(9) J. D. Berman and C. C. Price, *J. Amer. Chem. Soc.*, **79**, 5475 (1957).

nearly superimposable with that of **1b**, except for the absence of vinyl hydrogen absorption in **8**. The original assignment of stereochemistry to **1a** and **1b** can then be accepted with confidence.

Although we had hoped to be able to resolve **1a** and **1b** so as to obtain pure samples of each for study, this was not realized. Despite the fact that the two isomers appeared to differ slightly in boiling point (see Experimental Section), all of the vpc columns tested showed only a single symmetrical peak for the equimolar mixture. Because we did have one of the pure isomers in hand, however, and a mixture of both isomers whose ratio could be determined, we were able to carry out our planned studies on the rearrangement reaction.

When the vinyl bromide mixture (1:1) of **1a** and **1b** was treated with potassium *tert*-butoxide at 100° for 5 min, and then worked up in the usual manner,[1] a 2.2:1.0 mixture of 1-bromo-3,3-dimethylcyclopentene (**2a**) and 2-bromo-3,3-dimethylcyclopentene (**2b**) was produced in 72% yield (eq 3). (The aqueous phase yielded 24% inorganic bromide, and the remaining organic material appeared as a nonvolatile polymeric residue.) A clear preference for the migration of the less substituted carbon is shown by the preponderance of isomer **2a** in the reaction mixture. This preponderance became overwhelming (16:1) when the pure trans isomer **1a** was subjected to the reaction conditions (eq 4). Both compound **2a** and **2b** were stable under the reaction conditions.

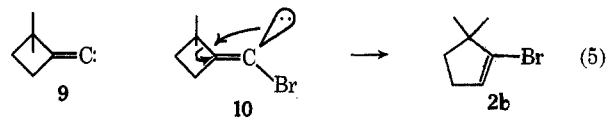


(3)

(4)

The assignment of structure to the two isomers, **2a** and **2b**, is based on nmr evidence. The isomers were easily resolved by vpc and could be analyzed separately. An unambiguous assignment could be made along several lines of evidence. First, the chemical shift of the allylic protons in **2a** occurred at δ 2.61 while those of isomer **2b** came at δ 2.21. The downfield shift for these protons in isomer **2a** is due to the adjacent bromine substituent. Second, the allylic protons in **2a** appear as a first-order pattern (triplet of doublets), while those in **2b** appear as a complex multiplet. A closer approach to first order is expected in **2a** because of the greater chemical shift difference for the allylic and nonallylic protons compared to that in **2b**. Finally, the $J_{\text{vinylic-allylic}}$ is smaller in **2a** than in **2b**, the order observed in cyclopentene itself.[10] (See the Experimental Section for details on the spectra.)

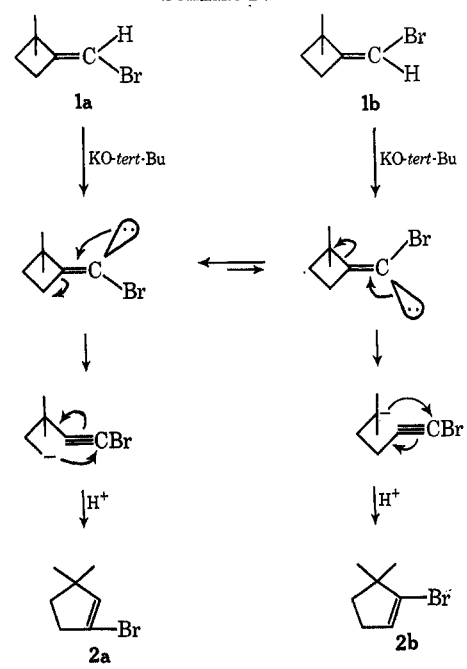
The results clearly indicate that the stereochemistry of the starting material is important in determining the ratio of products formed. A symmetrical intermediate such as the carbene **9** postulated in mechanism a is therefore untenable. The concerted carbanionic mechanism (mechanism b) is also ruled out as the carbanion **10** from the trans isomer **1a** ought to give rise to isomer **2b** (eq 5) which is the opposite to what is found. The



(5)

results can be accommodated by the cleavage–recombination mechanism (mechanism c) if a prior isomerization step is invoked as in Scheme IV. Without invoking this step one must assume that the trans isomer rearranges with a stereospecificity factor much greater than the cis isomer, an unlikely situation. More attractive is the process outlined where isomerization occurs before rearrangement, the trans isomer being favored, and the ring opening in each case being highly stereospecific as such trans elimination processes normally are. Presumably for steric reasons, the trans isomer **1a** rearranges at a rate faster than the cis isomer **1b** and also faster than the equilibration of the two isomeric carbanions.[11] Were this not the case, the same product distribution should obtain with both pure **1a** and the mixture of **1a** and **1b**.

SCHEME IV

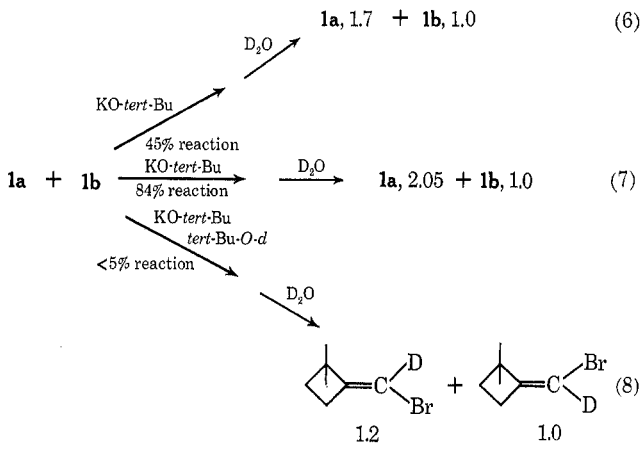


That isomerization does indeed occur under the reaction conditions was shown by allowing a 1.2:1.0 mixture of **1a** and **1b** to react with potassium *tert*-butoxide at room temperature for 10 min and then quenching the reaction with deuterium oxide. Under these conditions, 45% rearrangement had occurred. The starting vinyl bromide mixture was recovered and shown to consist of a trans/cis isomer ratio of 1.7:1.0 (eq 6). If one extrapolates to 100% reaction, the trans/cis ratio would be 2.2:1.0, which corresponds to the ratio of products **2a** and **2b** formed from the equimolar mixture of **1a** and **1b**. Similarly, quenching the reaction after

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

(11) We thank the referees for drawing our attention to this fact.

84% reaction gave recovered starting materials with a trans/cis ratio of 2.05:1.0 (eq 7). No measureable



amount of deuterium was incorporated into the starting material by quenching the reaction with deuterium oxide. This is not surprising as the concentration of anion at any given time is not expected to be high. Rather, a rapid equilibrium is probably established between starting material and anion followed by a slow, rate-determining rearrangement step.

In order to obtain evidence that the anion is formed reversibly, a 1.2:1.0 mixture of **1a** and **1b** was stirred with potassium *tert*-butoxide in deuterated *tert*-butyl alcohol for 2 hr (eq 8). Less than 5% rearrangement occurred under these conditions. The recovered starting material had not undergone any detectable isomerization (ratio of trans/cis held at 1.2:1.0) but had undergone complete exchange: no vinyl hydrogens were present in the nmr, and all vinylic couplings had disappeared. There is ample precedence in the literature for the *tert*-butyl alcohol–potassium *tert*-butoxide system effecting exchange without isomerization.[12]

The results obtained to date can best be explained by the elimination–addition (cleavage–recombination) mechanism outlined in Scheme IV. The fact that no acyclic products are found indicates that ring closure must be rapid relative to trapping by the *tert*-butyl alcohol or that the anion is not a completely free acyclic species. Further details on the mechanism of this unusual rearrangement must await additional experimental data.

Experimental Section[13]

***tert*-Butyl 2-(Dimethylamino)-3,3-dimethylcyclobutanecarboxylate.**[5]—*tert*-Butyl acrylate (36.0 g, 0.28 mol), *N*,*N*-dimethylisobutenylamine (75.0 g, 0.76 mol), and 100 ml of acetonitrile were heated at reflux under nitrogen for 120 hr. Acetonitrile and excess enamine were removed by atmospheric distillation, and the residue was distilled at reduced pressure to give 57 g (89%) of product, bp 66–70° (0.2 mm) [lit.[5] bp 45–47° (0.08 mm)].

***tert*-Butyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate.**[5]—*tert*-Butyl 2-(dimethylamino)-3,3-dimethylcyclobutanecarboxylate (56.6 g, 0.25 mol) was dissolved in 700 ml of a 2 *M* acetate buffer (pH 6), and the solution was cooled in an ice–water bath. To this was added dropwise with vigorous stirring 87 g (0.54 mol) of bromine. After complete addition (15 min), solid sodium bisulfite was added to destroy excess bromine. Zinc dust (90 g) was then added, and the mixture was allowed to warm to room temperature with vigorous stirring over 1 hr. The mixture was filtered, and the excess zinc was washed with water followed by ether. The filtrate was extracted with ether, and the ether extracts were washed successively with water, saturated sodium bicarbonate solution, water, and brine, and then dried over magnesium sulfate. Evaporation of the ether gave 38 g (77%) of crude product which was used directly for the next step.

2,2-Dimethylcyclobutanone.[5]—Crude *tert*-butyl 3,3-dimethyl-2-oxocyclobutanecarboxylate (30 g, 0.15 mol) was heated with 120 mg of *p*-toluenesulfonic acid monohydrate in a small distillation apparatus. Gas evolution began at 130°, and the product distilled. The 2,2-dimethylcyclobutane thus obtained (12.2 g, 81%) is pure enough for most purposes, bp 107–108° (740 mm) [lit.[5] bp 113–114° (760 mm)].

Ethyl 2,2-Dimethylcyclobutylideneacetate (3).—A 100-ml flask was equipped with a magnetic stirrer, pressure-equalizing dropping funnel, condenser, drying tube, and nitrogen inlet tube. The system was flushed with nitrogen, and 0.48 g (0.02 mol) of oil-free sodium hydride dispersion was placed in the flask followed by 20 ml of anhydrous monoglyme. To this was added dropwise 5.24 g (0.02 mol) of triethyl phosphonoacetate in 10 ml of monoglyme. After complete addition, the mixture was stirred for 15 min, and then 1.96 g (0.02 mol) of 2,2-dimethylcyclobutanone was added dropwise in 5 ml of monoglyme. The mixture was stirred at room temperature for 1 hr, during which time a gelatinous precipitate formed. Ice water was added, the mixture was extracted with ether, and the ether extracts were washed with several portions of water and then dried over magnesium sulfate. Evaporation of the ether and distillation of the residue at reduced pressure gave 2.55 g (90%) of essentially pure trans isomer: bp 41–42° (0.15 mm); ir (neat) 5.82, 5.97, 7.10, 7.31, 7.87, 8.45, 9.46, 9.62, 11.68 μ; nmr ($CDCl_3$) δ 1.25 (s, 6 H), 1.29 (t, 3 H), 1.87 (t, 2 H), 3.07 (m, 2 H), 4.12 (q, 2 H), 5.55 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.22; H, 9.61.

2,2-Dimethylcyclobutylideneacetic Acid (4).—Ester **3** (2.35 g, 0.014 mol) was refluxed with an aqueous ethanol solution of 1.2 g potassium hydroxide for 3 hr. The mixture was cooled and excess ethanol was removed *in vacuo*. Acidification with 6 *M* hydrochloric acid afforded 1.76 g (92%) of crude acid, mp 83–85°. Recrystallization from aqueous ethanol followed by sublimation at reduced pressure gave an analytical sample of the trans isomer: mp 89–90°; ir (Nujol mull) 5.88, 6.03 7.25, 7.35, 7.74, 7.84, 8.13, 8.25, 10.50, 11.56, 14.58 μ; nmr ($CDCl_3$) δ 1.25 (s, 3 H), 1.86 (t, 2 H), 3.08 (m, 2 H), 5.55 (m, 1 H), 11.34 (broad s, 1 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.72; H, 8.69.

2,2-Dimethyl-1-methylenecyclobutane (6).—A 100-ml flask was equipped with a magnetic stirrer, addition funnel, condenser, drying tube, and a nitrogen inlet tube. The system was flushed with nitrogen and then 0.48 g (0.02 mol) of oil-free sodium hydride dispersion was placed in the flask. To this was added dropwise 10 ml of anhydrous dimethyl sulfoxide (distilled from calcium hydride at 1 mm). After complete addition of the sulfoxide, the mixture was heated at 75° for 45 min and then cooled in an ice bath while 7.14 g (0.02 mol) of methyltriphenylphosphonium bromide in 25 ml of warm dimethyl sulfoxide was added dropwise. The resultant yellow-red suspension was stirred at room temperature for 15 min and then 1.96 g (0.02 mol) of 2,2-dimethylcyclobutanone in 2 ml of dimethyl sulfoxide was added dropwise; heat was evolved. The mixture was stirred at room temperature for 1 hr and then was subjected directly to flash distillation at 1 mm; all products were collected in Dry Ice cooled receivers. The distillate was then redistilled at atmospheric pressure through a short Vigreux column, the fraction boiling between 80–95° being collected. The product thus obtained was brominated directly without further purification. A vpc sample (Carbowax 20M, 80°) displayed ir (CCl_4) 3.22, 3.35, 3.45, 5.98, 6.84, 7.03, 7.25, 7.34, 11.36 μ; nmr (CS_2) δ 1.24 (s, 6 H), 1.73 (t, 2 H), 2.60 (m, 2 H), 4.57 (m, 2 H).

1-Bromo-1-bromomethyl-2,2-dimethylcyclobutane (7).—The crude 2,2-dimethyl-1-methylenecyclobutane obtained above (8

(12) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(13) Infrared spectra were recorded with a Perkin-Elmer Model 137 spectrophotometer. The nmr spectra were recorded with a Jeolco Model C-60H or Varian Associates HA 100 sectrometer, using tetramethylsilane as an internal standard. Vapor phase chromatographic analyses were performed on a Varian Aerograph Model 90-P3 chromatograph using a 10 ft × 0.25 in. 20% Carbowax 20M on 60–80 Chromosorb P or a 10 ft × 3/8 in. 3% SE-30 on 60–80 Chromosorb W column. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Galbraith Microanalytical Laboratories, Knoxville, Tenn.

g) was dissolved in 50 ml of methylene chloride with 5 g of anhydrous pyridine. At ice temperature and with stirring, bromine was added dropwise until no further decolorization occurred. Excess solvent was removed *in vacuo*, and then the residue was taken up in pentane and washed successively with aqueous sodium bisulfite, 2 *M* hydrochloric acid, and water, and dried, and the pentane removed. The residue was distilled at reduced pressure to give two fractions, bp 80–83° (0.40 mm) and bp 95–100° (0.15 mm); the latter was not identified. An analytical sample of 1-bromo-1-bromomethyl-2,2-dimethylcyclobutane (**7**) (vpc, SE-30, 100°) displayed ir (neat) 7.22, 7.31, 10.88, 11.16 μ; nmr ($CDCl_3$) δ 1.12 (s, 3 H), 1.38 (s, 3 H), 1.83 (m, 2 H), 2.50 (m, 2 H), 3.83 (s, 2 H).

Anal. Calcd for $C_7H_{12}Br_2$: C, 32.84; H, 4.73; Br, 62.57. Found: C, 32.90; H, 4.78; Br, 62.42.

1-Bromomethylene-2,2-dimethylcyclobutane (1a and 1b).—Dibromide **7** (7.5 g, 0.029 mol) and 2.0 g of potassium hydroxide in 100 ml of 95% ethanol was refluxed for 3 hr. Excess ethanol was removed *in vacuo*, and the residue was taken up in pentane and washed with water several times. The pentane layer was dried, and the pentane was removed by distillation through a short Vigreux column. Vacuum distillation of the residue afforded a rather broad-boiling set of fractions, bp 85–97° (22 mm), which corresponded to mixtures of the cis and trans isomers of slightly varying proportions. A total of 4.0 g (78%) of the mixture (*ca.* 1:1) was obtained: ir (neat) 3.23, 6.01, 7.23, 7.32, 7.81, 12.90, 13.66, 14.12 μ; nmr ($CDCl_3$) δ 1.23 (s, 6 H), 1.34 (s, 6 H), 1.75 (t, 4 H), 2.58 (m, 4 H), 5.62 (m, 1 H), 5.77 (m, 1 H). The ratio of isomers in a given sample could be easily determined by measuring the ratio of the methyl signals (δ 1.23, 1.34) or the ratio of the vinyl hydrogen signals (δ 5.62, 5.77) in the nmr.

Anal. Calcd for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.64. Found: C, 47.88; H, 6.37; Br, 45.89.

A small amount of a higher boiling fraction, bp 54–56° (0.15 mm), was obtained and identified as 2,2-dimethyl-1-ethoxy-1-ethoxymethylcyclobutane: ir (neat) 7.27, 7.38, 8.88, 9.00, 9.88 μ; nmr (CCl_4) δ 1.12 (t, 6 H), 1.70 (s, 6 H), 2.0–2.5 (m, 4 H), 3.31 (q, further split, 4 H), 3.85 (s, 2 H).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 71.23; H, 11.60.

Pure trans isomer **1a** was obtained in the following manner. Unsaturated trans acid **4** (2.46 g, 0.0176 mol) was dissolved in pentane and added dropwise to a suspension of 0.422 g (0.0176 mol) of oil-free sodium hydride dispersion in pentane. The mixture was stirred at room temperature for 15 min and then the pentane was removed *in vacuo* to give the dry acid salt. This salt was suspended in 100 ml of anhydrous dimethylformamide (distilled from calcium oxide), and, with vigorous stirring 2.82 g (0.0176 mol) of bromine was added dropwise. The color discharge was slow. After complete addition of the bromine, all of the suspended solid had dissolved. The mixture was poured into water–pentane, and the pentane layer was washed successively with sodium bisulfite, sodium bicarbonate, and water. The pentane layer was dried, and the pentane was removed by distillation through a short Vigreux column. The residue was flash distilled. Two major products were formed in this reaction; the desired one, *trans*-1-bromomethylene-2,2-dimethylcyclobutane (**1a**), was collected by vpc (Carbowax 20M, 100°). The ir of this single isomer was very similar to that of the mixture of isomers described above. The nmr ($CDCl_3$) clearly showed the presence of only one isomer: δ 1.23 (s, 6 H), 1.75 (t, 2 H), 2.58 (m, 2 H), 5.77 (m, 1 H).

Dibromomethylenecyclobutane (8).—1-Bromomethylene-2,2-dimethylcyclobutane (mixture of **1a** and **1b**) (0.35 g, 0.002 mol) was dissolved in 5 ml of methylene chloride and 0.16 g (0.002 mol) of anhydrous pyridine was added. With stirring, 0.32 g (0.002 mol) of bromine was added dropwise, and the mixture was stirred at room temperature for 24 hr. It was then extracted with aqueous acid, the methylene chloride layer was dried (magnesium sulfate), and the solvent was removed *in vacuo*. The residue was refluxed with a solution of 0.2 g potassium hydroxide in 95% ethanol for 1 hr. The mixture was then poured into ice-water and extracted with pentane. After drying, the pentane was removed and the residual yellow liquid purified by vpc (SE-30, 150°) to give dibromomethylenecyclobutane: ir (neat) 6.01, 7.25, 7.34, 12.13, 12.71 μ; nmr (CCl_4) δ 1.33 (s, 6 H), 1.75 (m, 2 H), 2.57 (m, 2 H).

Anal. Calcd for $C_7H_{10}Br_2$: C, 33.10; H, 3.97. Found: C, 33.47; H, 4.12.

Reaction of 1-Bromomethylene-2,2-dimethylcyclobutane with Potassium *tert*-Butoxide. General Procedure.[1]—In a flask equipped with a reflux condenser, drying tube, nitrogen inlet tube, and rubber septum was placed the potassium *tert*-butoxide (slight excess). The system was flushed with nitrogen, and the butoxide was heated to the desired temperature; the vinyl bromide was injected *via* a syringe under the surface of the butoxide; and the temperature was maintained for the desired period of time. The mixture was cooled, and water was added and extracted with pentane. The aqueous phase was analyzed for inorganic bromide (silver nitrate) and the pentane layer for organic products. The pentane was removed by distillation through a short Vigreux column, and the residue was flash distilled at reduced pressure. Carbowax 20M at 80° was used for chromatographic analysis of the distillates.

A. With 1:1 Mixtures of 1a and 1b.—The vinyl bromide mixture (1.75 g, 0.010 mol) was injected into 1.23 g (0.011 mol) of potassium *tert*-butoxide at 100°, and the temperature was maintained for 5 min. The mixture was processed in the usual manner. Flash distillation afforded 1.25 g (72%) of a 2.2:1 mixture of 1-bromo-3,3-dimethylcyclopentene (**2a**) and 2-bromo-3,3-dimethylcyclopentene (**2b**). The aqueous phase yielded 24% inorganic bromide. Repetition of this reaction several times gave the same results.

The two isomeric bromides were separated by vpc (Carbowax 20M, 80°) and identified by spectroscopic data. 1-Bromo-3,3-dimethylcyclopentene (**2a**) displayed ir (neat) 3.22, 6.08, 6.88, 7.28, 7.36, 7.60, 8.33, 9.05, 9.76, 11.90, 12.56, 13.52 μ; nmr ($CDCl_3$), 100 MHz) δ 1.07 (s, 6 H), 1.73 (distorted t, 2 H), 2.61 (t of d, 2 H), 5.63 (t, 1 H). 2-Bromo-3,3-dimethylcyclopentene (**2b**) displayed ir (neat) 3.21, 6.07, 6.87, 7.25, 7.34, 7.58, 9.01, 10.16, 10.53, 11.06, 11.48, 12.20, 12.70, 14.33 μ; nmr ($CDCl_3$, 100 MHz) δ 1.07 (s, 6 H), 1.80 (t, further split, 2 H), 2.21 (complex m, 2 H), 5.71 (t, 1 H).

Anal. Calcd for $C_7H_{11}Br$ (mixture of both isomers): C, 48.02; H, 6.33; Br, 45.64. Found: C, 48.20; H, 6.46; Br, 45.41.

B. With Pure Trans Isomer 1a.—This reaction, repeatedly carried out in an identical manner with that of the isomer mixture, afforded a mixture of 1-bromo-3,3-dimethylcyclopentene (**2a**) and 2-bromo-3,3-dimethylcyclopentene (**2b**) in an average relative ratio of 16:1.

Reaction of 1-Bromo-3,3-dimethylcyclopentene (2a) and 2-Bromo-3,3-dimethylcyclopentene (2b) with Potassium *tert*-Butoxide.—A 2.2:1.0 mixture of **2a** and **2b** was subjected to an excess of potassium *tert*-butoxide at 100° for 10 min. After work-up of the mixture in the usual fashion, the starting vinyl bromide mixture was recovered unchanged.

Isomerization Studies with 1-Bromoethylene-2,2-dimethylcyclobutane (1a and 1b).—A mixture of isomeric bromides consisting of a trans/cis ration of 1.2:1.0 was stirred with a slight excess of potassium *tert*-butoxide suspended in hexane at room temperature for 10 min. The reaction was quenched with deuterium oxide and worked up as usual. Vpc showed 45% rearrangement had occurred. Starting material was recovered by vpc (Carbowax 20M, 100°) and analyzed by nmr which showed a new trans/cis ratio of 1.7:1.0. Extrapolation to 100% reaction gave a trans/cis ratio of 2.2:1.0. Repetition of this experiment to 84% reaction gave recovered starting material with a trans/cis ratio of 2.05:1.0. There was no detectable decrease in vinyl hydrogen intensity.

Deuterium Exchange Studies with 1-Bromomethylene-2,2-dimethylcyclobutane (1a and 1b).—A mixture of isomeric bromides with a trans/cis ratio of 1.2:1.0 was stirred with a slight excess of potassium *tert*-butoxide in *tert*-butyl alcohol-*O*-*d* at room temperature for 75 min then at 50° for 1 hr. Work-up showed less than 5% rearrangement had occurred. The starting material was recovered (vpc, Carbowax 20M, 100°) and subjected to nmr analysis. The trans/cis ratio was not measurably changed from 1.2:1.0, but both vinyl hydrogen signals had disappeared as well as all vinylic couplings to other signals. There was no detectable allylic exchange.

Registry No.—**1a**, 27787-12-8; **1b**, 27787-13-9; **2a**, 27787-14-0; **2b**, 27787-15-1; *trans*-**3**, 27932-04-3; *trans*-**4**, 27787-16-2; **6**, 27787-17-3; **7**, 27787-18-4; **8**, 27787-19-5; potassium *tert*-butoxide, 865-47-4; 2,2-dimethyl-1-ethoxy-1-ethoxymethylcyclobutane, 27787-20-8.

Acknowledgments.—This work was supported by the Petroleum Research Fund, administered by the American Chemical Society. The author wishes to express her thanks to Dr. T. Wittstruck, Worcester Foundation for Experimental Biology, for the 100-MHz nmr spectra, to Mr. S. Baniukiewicz for the 60-MHz nmr spectra, and to Dr. P. T. Inglefield for valuable discussions concerning these spectra.

Cyclopropanes. XXX. Reductive Cleavage of Cyclopropane Rings[1]

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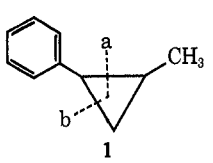
Received September 14, 1970

1,1-Biphenylene-2-methylcyclopropane (**5**) was synthesized and subjected to reductive cleavage with sodium and lithium in liquid ammonia, sodium in glyme, sodium naphthalide in glyme, and by controlled potential electrolysis in acetonitrile at a mercury cathode. The reductive cleavage of **5** yielded under all conditions a mixture of 9-propylfluorene (**6**) and 9-isopropylfluorene (**7**) with the isomer ratio of **6**:**7** varying from 96:4 to 81:19. The cleavage of the cyclopropane ring is in the direction of the more substituted carbon (less thermodynamically stable carbanion), and the change in isomer ratio is ascribed to a solvent effect.

The reductive cleavage of the cyclopropyl ring system by solutions of alkali metals in liquid ammonia has been receiving a great deal of current interest. It has been shown, originally by Boord and coworkers[2] and more recently by Norin,[3] Dauben,[4] and Fraisse-Jullien,[5] that a carbonyl group attached to the ring was necessary to observe the ring opening. House[6] extended this to cyclopropylcarboxylic esters. More recently it was demonstrated that a phenyl substituent[7] would also cause the cyclopropyl ring to undergo reductive cleavage.

As data accumulated it became apparent that a number of factors controlled the direction of ring opening, among them being the ability of the π orbital of the carbonyl or phenyl group to overlap with an adjacent cyclopropyl bond.[3,4] This postulate accounts well for the regiospecific mode of ring opening in fused bicyclic systems.[3,4] Other factors that are considered to be important are electronic and steric[4a,6,7b,d] in nature and have been shown to be significant factors in systems in which dynamic conformational isomers are involved.[4b,7d] For example, in the cases studied by Staley,[7d] the geometric isomers, *cis*- and *trans*-1-methyl-2-phenylcyclopropane (**1**), yielded different ratios of cleavage product



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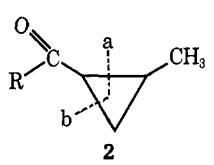

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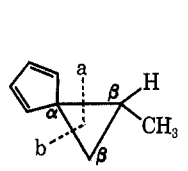
with the trans isomer giving mainly cleavage of bond b and the cis isomer giving predominant cleavage of bond a. A similar observation was made by Dauben[4b] for *cis*- and *trans*-alkyl-2-methylcyclopropyl ketones (**2**). Both groups of workers rationalized their results on the bases of steric and electronic factors.

Of particular interest were the results of the reduction of 1-methylspiro[2.4]hepta-4,6-diene (**3**) in which the cleavage of bond b is favored by a ratio of 5:1.[7d] Due



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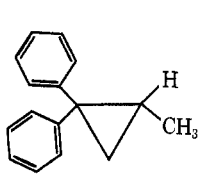

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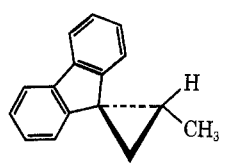

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to the rigidity of the structure there are no preferential conformational isomers possible (*vide supra*). The preference for bond b cleavage was taken as further support of the electronic influence on the reaction in which negative charge is believed to accumulate on the β carbon in the activated complex and with the methyl group exerting a destabilizing effect.

In our work[7a] on the reductive cleavage of 1-methyl-2,2-diphenylcyclopropane (**4**) it was shown that bond a was cleaved in preference to b by a factor of *ca.* 5. This result was rationalized on the basis, *inter alia*, that a methyl group would stabilize the ion-radical intermediate which has radical character at the β carbon atom and the anion localized on the diphenylcarbinyl atom. It was pointed out[7d] that steric factors are also playing an important role in the reduction of **4**. In order to help evaluate the role of steric factors, the electronically analogous system, 1,1-biphenylene-2-methylcyclopropane (**5**), was chosen for investigation. This system not only has the phenyl groups frozen but they are in the preferred bisecting conformation[8] as well.

Syntheses and Reactions.—The synthesis of **5** was accomplished by standard procedures. The addition of 9-diazofluorene to methyl acrylate produced methyl 2,2-biphenylenecyclopropanecarboxylate in 65% yield. Reduction with lithium aluminum hydride produced the corresponding carbinol (88%) which was converted to the tosylate (98%), and the tosylate was reduced to **5** in 78% yield with lithium aluminum hydride.

(1) Support of this work by grants from the Petroleum Research Fund of the American Chemical Society and the National Science Foundation is gratefully acknowledged.

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