Stereochemistry of Free Radical Ring Cleavage of *cis*-1,2,3-Trimethylcyclopropane by Bromine

Gordon G. Maynes and Douglas E. Applequist*

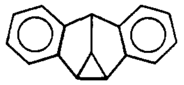
Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received July 28, 1972*

Abstract: The free radical ring cleavage of *cis*-1,2,3-trimethylcyclopropane by bromine has been shown to proceed with inversion of configuration at one center and by a nonstereospecific reaction at the other center. These conclusions are based on the identification of (*S*)-*meso*-3-methyl-2,4-dibromopentane and of an almost equal amount of *dl*-3-methyl-2,4-dibromopentane as the only dibromide products of the reaction.

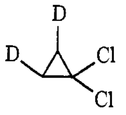
Free radical bimolecular substitution reactions on carbon (SH2) have been sought for many years.[1] The process is electronically intermediate between nucleophilic and electrophilic substitutions. An important question, then, is whether the radical reaction would proceed with inversion of configuration at the attacked carbon, in analogy to nucleophilic displacements,[2] or with retention, as demonstrated for some electrophilic displacements.[3]

In the case of 9,10-dehydrodianthracene, the proven free radical reaction with bromine proceeds with inversion.[4] The aim of the present research was to study a system in which the retention pathway is not disfavored, unlike this example. Since the ring cleavage reactions of cyclopropane derivatives with chlorine,[5] bromine,[6] and iodine[7] are believed to be examples of SH2 reactions,[8] the symmetrical *cis*-1,2,3-trimethylcyclopropane[9] (**1**) was chosen as the substrate. The advantages of this molecule are that it has no electronic bias and that any intermediate radicals are not constrained to fixed orientations (in which approach to one side may be restricted severely) by the presence of additional ring structure.

While this work was in progress, two reports were published in which radical additions to dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene[10] (**2**) and 1,1-dichloro-2,-3-dideuteriocyclopropane[11] (**3**) were reported to proceed with inversion of configuration at both and one center(s), respectively.



2

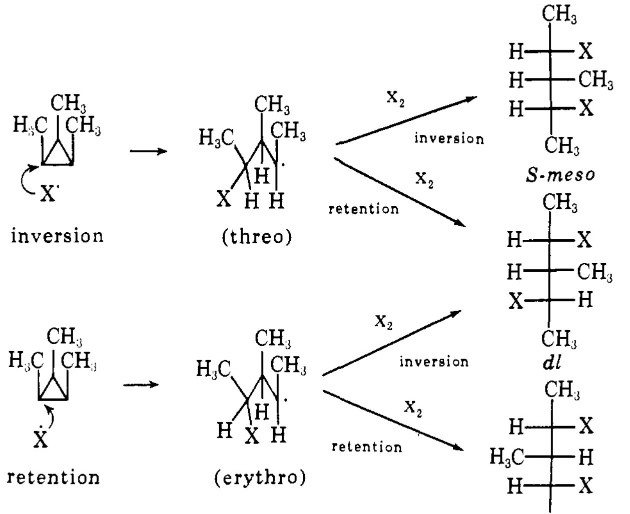


3

Both of these molecules suffer from some degree of steric and electronic bias, the importance of which has not been assessed. In addition, isomer stability controls were not conducted in the case of **2**.[10]

For *cis*-1,2,3-trimethylcyclopropane, the stereochemistry at both reaction centers can be inferred from the products. The three unique paths of reaction are outlined in Scheme I. With a symmetrical adding species such as bromine, information as to the order of two different stereochemical results is lost (*e.g.*, the inversion–retention pathway could take place with either step first). Naturally, a random reaction at one center leads to a mixture of two products (*e.g.*, inversion-random gives *S-meso* and *dl* derivatives).

Scheme I



The classical synthesis of the desired substrate,[9a,b] zinc reduction of 3-methyl-2,4-dibromopentane, was attempted but was found (in agreement with the observation of other workers[9c]) to give impractically large amounts of olefinic by-products. The method which was finally chosen was the iodide-promoted zinc reduc-

---

[1] K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, pp 72–90.

[2] A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

[3] (a) H. B. Charman, E. D. Hughes, and C. Ingold, *J. Chem. Soc.*, 2530 (1959); (b) F. R. Jensen, *J. Amer. Chem. Soc.*, **82**, 2469 (1960); D. J. Cram and P. Haberfield, *ibid.*, **83**, 2354 (1961).

[4] D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

[5] (a) G. Gustavson, *J. Prakt. Chem.*, **42**, 495 (1890); (b) G. Gustavson, *ibid.*, **43**, 396 (1891); (c) J. D. Roberts and P. H. Dirstine, *J. Amer. Chem. Soc.*, 67, 1281 (1945); (d) P. G. Stevens, *ibid.*, 68, 620 (1946); (e) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962); (f) A. J. Davidson and A. T. Bottini, *J. Org. Chem.*, **34**, 3642 (1969).

[6] (a) R. A. Ogg and W. J. Priest, *J. Amer. Chem. Soc.*, 60, 217 (1938); (b) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *ibid.*, **61**, 2139 (1939); (c) B. H. Nicolet and L. Sattler, *ibid.*, **49**, 2066 (1927); (d) A. F. Wagner, N. E. Wolff, and E. S. Wallis, *J. Org. Chem.*, **17**, 529 (1952); (e) S. J. Cristol and R. T. LaLonde, *J. Amer. Chem. Soc.*, **80**, 4355 (1958); (f) H. G. Kuivila, S. C. Caywood, W. F. Boyce, and F. L. Langevin, Jr., *ibid.*, 77, 5175 (1955); (g) R. T. LaLonde, P. B. Ferrara, and A. D. Debboli, Jr., *J. Org. Chem.*, **37**, 1094 (1972); (h) H. W. Pouncey, Jr., Ph.D. Thesis, Syracuse University, Syracuse, N. Y., 1962.

[7] R. A. Ogg and W. J. Priest, *J. Chem. Phys.*, 7, 736 (1939).

[8] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 192.

[9] (a) N. Zelinsky and J. Zelikow, *Chem. Ber.*, **34**, 2856 (1901); (b) R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 77, 1751 (1955); (c) P. A. Waitkus, E. B. Sanders, L. I. Peterson, and G. W. Griffin, *ibid.*, **89**, 6318 (1967).

[10] B. B. Jarvis, *J. Org. Chem.*, **35**, 924 (1970).

[11] J. H. Incremona and C. J. Upton, *J. Amer. Chem. Soc.*, **94**, 301 (1972).

tion of 3-methylpentane-2,4-diol ditosylate[12] in the presence of suitable complexing agents for zinc(II) to retard rearrangement.[13] The small amount of olefins formed was easily removed by selective bromination in aqueous 1-propanol. (Permanganate oxidation was found to destroy both olefins and cyclopropanes at comparable rates.) The two cyclopropane isomers could then be separated by preparative-scale vapor-phase chromatography (vpc) or, if a large amount of the mixture was available, by careful distillation through a packed column. (Spinning band distillation has been reported[14] to give facile separation.)

Bromination of Trimethylcyclopropanes. The optimum condition for bromination of either isomer of 1,2,3-trimethylcyclopropane was found to be irradiation of a stirred solution of the reactants in carbon tetrachloride. Unless a tenfold excess of *trans*-**1** or a twofold excess of the more reactive cis isomer was used, a small amount ($\sim$10%) of 2,3,4-tribromo-3-methylpentane was formed.[15] Unless the reactivities of the 3-methyl-2,4-dibromopentanes initially formed are not the same, this secondary bromination confirms the expected higher rate of reaction for the more strained *cis*-**1** ($\sim$5 times faster).

In the dark, a very slow reaction was observed. This gave a complex mixture of products which could be interpreted in terms of a slow electrophilic reaction. In the presence of isoamyl nitrite the rate of reaction in light was also sharply reduced. These data help to support the free radical nature of the bromination.

Product Analysis. Stereochemistry. The nmr spectra of the cyclopropane bromination products gave rise to resonances in the region δ 4.1–4.8, which correspond to the protons α to bromine. Four clear multiplets (at δ 4.10, 4.19, 4.35, and 4.77) were observed in the spectrum of the product from bromination of *trans*-**1** and three (at δ 4.10, 4.35, and 4.77) were found in that from bromination of *cis*-**1**.

The synthesis of 4-bromo-3-methyl-2-pentene from *cis*- or *trans*-3-methyl-3-penten-2-ol led to the same mixture of allylic halide geometrical isomers, regardless of the reagent used to affect the conversion, the ratio of cis:trans being 10:1.[16]

The free radical addition of hydrogen bromide to the equilibrium mixture of allylic bromides gave dibromides with resonances at δ 4.10, 4.19, and 4.77 (with a trace of the isomer which gives a resonance at δ 4.35). The only resonances common to all three spectra are those at δ 4.10 and 4.77. Therefore, these arise from the *dl* pair. The other two multiplets, at δ 4.19 and 4.35, arise from the two *meso* forms, the identities of which are discussed subsequently. (The other resonances in the spectra, as reported in the Experimental Section, were assigned through similar logic.)

These data permit a partial solution of the mechanism. The fact that the resonances from one isomer are missing in the spectrum of the *cis*-**1** bromination product indicates that the reaction is stereospecific at one reaction center, and the presence of resonances corresponding to the *dl* pair and one *meso* form indicates that the reaction is random at the other center. In other words, any complexing between cyclopropane and bromine which may be occurring does not put the bromine in a position where it can bond to the developing radical in any concerted and specific manner. (Unfortunately, these results do not unequivocally rule out complexing, as one could propose a variety of fanciful rationales to account for this behavior. Kinetics is still the only method to get an accurate count of the number of bodies in the transition state, and even here limitations are met in discussion of the role of solvent in any chemical reaction. However, we must say that the radical here is behaving in the manner of a classically "free" radical.) This result is significant, since no study has demonstrated steric control at one center and not at the second (in the study of 1,1-dichlorocyclopropane[11] the second could not be determined).

With the nature of the reaction at one carbon thus on firm ground, it then became necessary to identify the *meso* form arising from bromination of *cis*-**1**, since this would permit a decision between retention and inversion at the other center. The fact that different *meso* forms were produced by this reaction and by radical addition of hydrogen bromide to predominantly *cis*-4-bromo-3-methyl-2-pentene seemed indicative of inversion, since trans addition to the allylic system would have given the *R-meso* and the *dl* pair, leaving the cyclopropane-derived isomer to be the *S-meso*. Failure to synthesize *trans*-4-bromo-3-methyl-2-pentene prevented demonstration that this could not be merely a stereoselective[17] process (giving the same predominant product regardless of starting material) so an alternative was sought for unequivocal demonstration of the identity of the *R*- and *S-meso* dibromides.

The hydroboration followed by peroxide cleavage of the known[18] *cis*- and *trans*-3-methyl-3-penten-2-ol isomers (a process which has been shown to add the elements of water to the same side of an olefin[19]) gave mixtures of the individual *R*- and *S-meso* isomers accompanied by the *dl* pair, as shown in Scheme II. The *meso* isomers could then be separated from the *dl*-pair as the 1,3-dioxanes, and the identity of each was confirmed by the relative magnitudes of the coupling constants between the ring protons.[20] The extraordinary stability of these dioxanes precluded facile isolation of the pure *meso* diols, but this was an unnecessary refinement.

Conversion of each mixture of alcohols to the ditosylates, and treatment of the crude ditosylates with sodium azide in HMPA gave the diazides (*S* + *dl* diol gave *R* + *dl* diazide; *R* + *dl* diol gave *S* + *dl* diazide, assuming inversion). Treatment of the dibromide mix-

---

[12] R. P. Mariella and K. H. Brown, *J. Org. Chem.*, **34**, 3191 (1969).

[13] (a) H. B. Hass, E. T. McBee, G. E. Hinds, and B. W. Glutenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936); (b) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Org. Chem.*, **23**, 1715 (1958).

[14] C. H. DePuy, private communication.

[15] (a) P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, **86**, 3334 (1964); (b) W. Thaler, *ibid.*, **85**, 2607 (1963); (c) M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, 20, 1430 (1950); (d) J. G. Traynham and W. G. Hines, *J. Amer. Chem. Soc.*, **90**, 5208 (1968); (e) W. C. Danen and R. L. Winter, *ibid.*, **93**, 716 (1971); but see (f) D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, **93**, 5846 (1971), and references therein.

[16] G. G. Maynes, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1972.

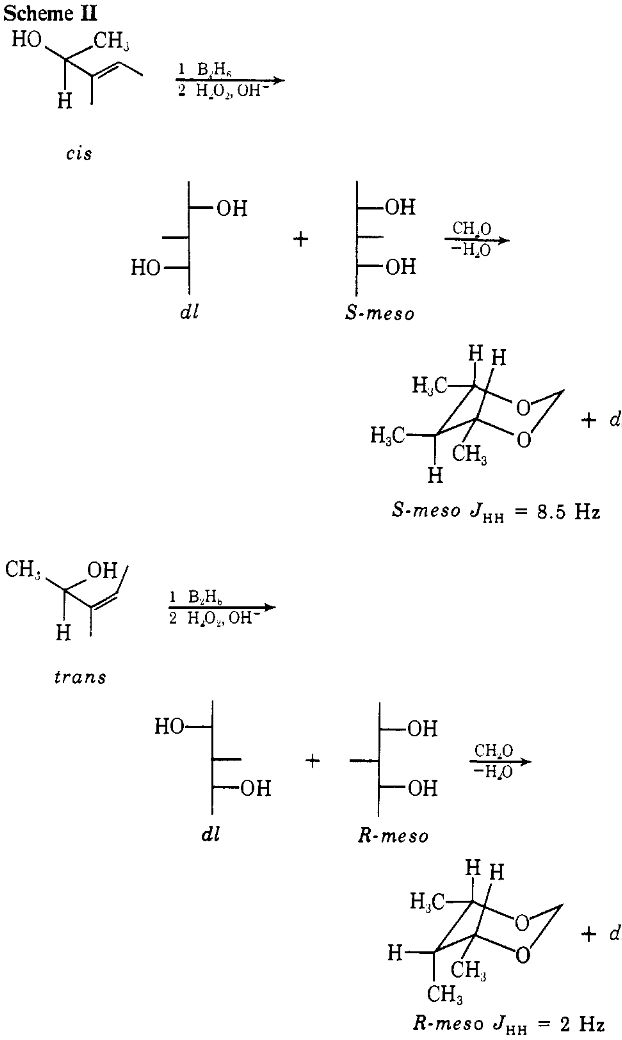
[17] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 434–446.

[18] H. O. House and R. S. Ro, *J. Amer. Chem. Soc.*, **80**, 2428 (1958).

[19] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

[20] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 144.

Scheme II



ture formed from *cis*-trimethylcyclopropane with potassium azide in aqueous acetone gave the *dl* diazide and the *R-meso* form. Thus, the *meso* dibromide must have been of the *S* configuration. Although the presence of impurities and severe spinning side bands in the spectrum preclude observation of less than 5% of the *S-meso* diazide, the spectrum of the starting material shows clearly that only two isomers (>99%) were present. A different mixture of diazides was obtained by treatment of dibromides from *trans*-trimethylcyclopropane with potassium azide. Although differing rates of substitution and of elimination for each isomer make the proportions of diazide products not representative of the isomeric composition of the starting dibromides (quantitatively), the fact that this second product mixture is radically different from the first precludes the possibility of bromide-catalyzed equilibration of the dibromides prior to azide displacement. The above series of reactions is outlined in Scheme III.

The dibromide mixtures obtained from bromination of *cis-* or *trans*-**1** were equilibrated with sodium bromide in HMPA. The dibromides isolated had undergone no positional isomerization, but the *R-meso* isomer, the missing or minor isomer in the two mixtures, respectively, had become the predominant *meso* form. These data clearly show that neither of the bromination product mixtures has the composition expected at thermodynamic equilibrium.

In summary, the bromination of *cis*-trimethylcyclopropane has been shown to proceed by inversion at one center, by virtue of the identification of one of the bromination products as (*S*)-*meso*-3-methyl-2,4-dibromopentane and the absence (<1%) of the *R-meso* form. This is analogous to the behavior observed in the chlorination of 1,1-dichlorocyclopropane,[11] the only other simple (nonpolycyclic) system for which a stereochemical conclusion has been drawn. An intermediate radical is proposed to be formed by this inversion which is free in the classical sense; that is, it reacts with almost equal probability on either face. This was demonstrated by the spectral identification of an equal amount of the *dl*-3-methyl-2,4-dibromopentane. That this bromination is a radical reaction is further substantiated by the observation that it fails to take place in the dark and is inhibited by isoamyl nitrite.

Experimental Section

Nuclear magnetic resonance (nmr) spectra were recorded on Varian T-60, A-60A, HA-100, or HR-220 instruments. Chemical shifts are expressed in parts per million relative to tetramethylsilane, which is used as an internal standard and assigned the value δ 0 ppm.

Vapor-phase chromatography (vpc) was done on a F & M Model 300 for analytical applications, and preparative scale separations were made using a Varian Aerograph Model 700. Both of these instruments were equipped with differential thermal conductivity detectors. Helium was used as the carrier gas, and separations were effected with the following columns: (A) 3 m × 0.65 cm 20% diisodecyl phthalate on 60–80 mesh Chromosorb P; (B) 3 m × 0.94 cm 20% diisodecyl phthalate on 60–80 mesh Chromosorb P; (C) 3 m × 0.65 cm 5% FFAP (Carbowax modified with nitroterephthalic acid) on 60–80 mesh AW/DMCS Chromosorb G; (D) 4 m × 0.94 cm FFAP on 60–80 mesh Chromosorb P. All columns were made of coiled copper tubing. The compositions of any mixtures are reported based on the integrated area under the appropriate chart peak, and are uncorrected for differences in thermal conductivity.

All melting points were taken on a Buchi "Schmeltzpunktbestimmungsapparat;" these and boiling points are uncorrected.

Those spectra recorded by the personnel of the University of Illinois School of Chemical Sciences are acknowledged; all analyses were done by Mr. J. Nemeth and Associates, also at the University of Illinois.

Materials. "Commercial" 3-methyl-2,4-pentanediol refers to that purchased from K and K Chemical Co., which was distilled before use. Otherwise, this compound was prepared by standard procedures.[9b] All chemicals and solvents were reagent grade, except as noted, and were used without purification, except as noted. All ground glass joints were lubricated with Dow Corning high-vacuum silicone lubricant.

3-Methylpentane-2,4-diol ditosylate was synthesized by addition of 1 kg of *p*-toluenesulfonyl chloride to a stirred solution of 160 g of commercial 3-methylpentane-2,4-diol in 4 pints of pyridine, which had previously been cooled to 0°. The reaction mixture was stored at +4° for 1 week and was poured into 12 l. of ice and water (this was done in 1/4 scale batches). The resulting resin was taken up in chloroform, and water and water-soluble impurities were removed. The chloroform was removed, and the resulting solid was recrystallized from methanol, yield 80%, mp 99–100°.

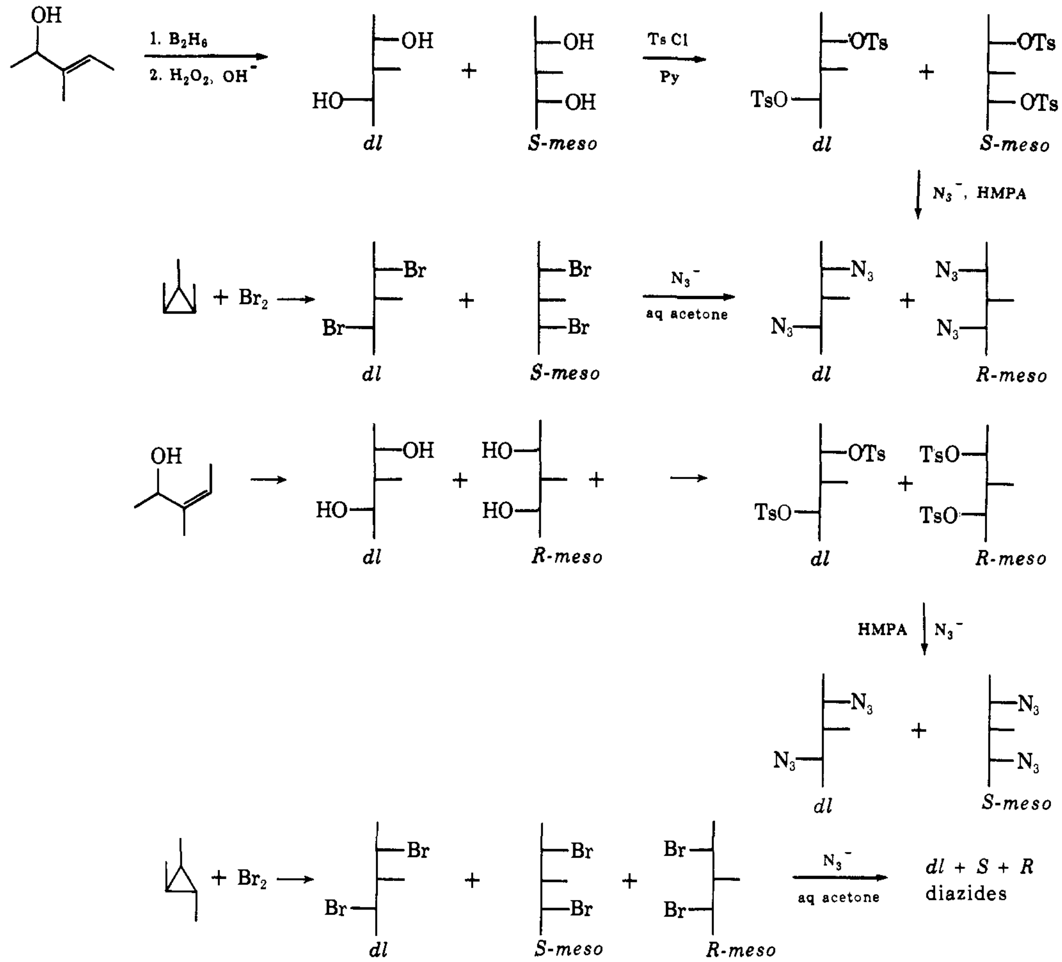
Anal. Calcd for $C_{20}H_{26}S_2O_6$: C, 56.33; H, 6.10; S, 15.02. Found: C, 56.36; H, 6.11; S, 14.85.

Reductive Cyclization of 3-Methyl-2,4-pentanediol Ditosylate. The ditosylate, 4.26 g, was added from a flask through Gooch tubing to a mechanically stirred suspension of 40 g of Mallenkrodt AR zinc dust, 5 g of sodium iodide, and 15 g of sodium carbonate in 100 g of acetamide at 140–150°. The products were allowed to distil out of the reaction flask as they formed and were trapped in two vessels, the first cooled to 0° and the second to −78°. The apparatus was purged with nitrogen at the end of the reaction, and the hydrocarbon mixture which had collected in the traps was washed with water and with brine, and the composition thereof was determined by glpc on column A at 110°.

The usual composition was found to be 60% *trans*-**1**, 16% *cis*-**1**, 6% 3-methyl-2-pentene, and 18% 3-methyl-1,3-pentadiene.

Hydrocarbon Product Identifications. The four principle prod-

Scheme III



ucts of zinc cyclizations reported herein were separated on column B at 130°. In the order of their elution these are the following.

(a) **trans-1,2,3-Trimethylcyclopropane:** nmr δ −0.295 (m, 1 H), 0.372 (m, 2 H), 0.985 (m, 9 H); mass spectrum parent *m/e* 84, base *m/e* 41; bp 56.5° (735 Torr); $n_D^{22.5}$ 1.386 (lit.[9b] bp 59.7° (760 Torr); n_D^{20} 1.387).

(b) **3-Methyl-2-pentene.** This compound was identified by comparison of its ir spectrum with that of an olefin prepared by dehydration of 3-methylpentan-3-ol[21] and with standard spectra.[22] The cis and trans isomers were not separated.

(c) **cis-1,2,3-Trimethylcyclopropane:** nmr δ 0.9, broad singlet; mass spectrum parent *m/e* 84, base *m/e* 41; bp 71.5° (735 Torr); $n_D^{22.5}$ 1.403 (lit.[9b] bp 65–67° (760 Torr)); n_D^{20} 1.393–1.396; lit.[9c] nmr τ 9.15, mass spectrum parent *m/e* 84; the ir was identical with that reported by these[9c] authors. This report evidently involves a compound seriously contaminated with olefinic impurities.

(d) **3-Methyl-1,3-pentadiene:** nmr δ 1.7 (m, 6 H), 5.0 (m, 2 H), 5.55 (m, 1 H), 6.4 (m, 1 H); ir 3090 (vinyl C–H), 1610, 1645 (conj diene C=C str), 990, 894 (vinyl C–H bend), 833 cm^{-1} (trisubstituted C–H bend) (lit. spectrum (Marvel and Williams[23]) uv λ max 228.5 nm (hexane); calcd λ_{max} 227 nm). The same compound could be prepared by heating 3-methylpentane-2,4-diol in HMPA: bp 75–78.5° (733.5 Torr), n_D^{23} 1.445 (lit.[24] bp 76–79°, $n_D^{16.5}$ 1.454).

Olefin Removal. Treatment with Bromine in Aqueous 1-Propanol. A solution of 15 ml of water in 50 ml of 1-propanol was cooled to +3° in an ice bath, and 6.6 g of hydrocarbon mixture was dissolved therein. The olefins present were then titrated with a solution of 0.5 *M* bromine in 2.0 *M* aqueous sodium bromide. The color was fading noticeably more slowly after the addition of 67.2 ml of titrant, so the addition of bromine was discontinued. The resulting clear solution, which had separated into two phases, was heated to distil the hydrocarbons through a 20-cm wire-spiral column. When the temperature of the distillate reached 87°, distillation was stopped, and the product was washed with water and with brine. Recovery was 3.9 g, 59%.

Separation of Isomeric 1,2,3-Trimethylcyclopropanes. Initially, all separations were done on column B at 130°, and the isomers were trapped at −78°. When larger quantities became available, the pure isomers could be obtained by careful distillation at atmospheric pressure through a 127 cm × 1.5 cm column packed with single glass helices. The trans isomer is obtained first, bp 58°, then an intermediate fraction containing both isomers, and then the cis isomer, bp 71°.

Bromination of 1,2,3-Trimethylcyclopropane. (a) Approximate 1:1 Molar Ratio. A solution of 1.81 g of bromine (0.0113 mol) in 5 ml of Spectrograde carbon tetrachloride was added to a stirred solution of 1.00 g of the appropriate cyclopropane isomer in 7 ml of the same solvent. The Pyrex reaction vessel was cooled in an ice bath and illuminated by two 300-W incandescent bulbs from a distance of about 10 cm before the reactants were combined. The temperature of the reaction mixture rose to +6° during the reaction. When the color of the bromine had been discharged (∼0.5 hr for *trans*-**1**, ∼10 min for *cis*-**1**), the solvent and evolved hydrogen bromide were removed on the Rota-vap, and the residue was chromatographed on silica gel and eluted with carbon tetrachloride, yield 70%, giving one peak on the vpc (column C, 130°). In an alternative work-up, the product solution was first washed with water and with brine before concentration and chromatography. This made no difference in yield or product composition. The products of several runs were combined and distilled. The major product, bp 64° (3.9 Torr) (70%, 96% of volatile products by vpc),[9b] lit. bp 98° (36 Torr), was identified by nmr as a mixture of 2,4-dibromo-3-methylpentane isomers. This material was then used as "authentic" 2,4-dibromo-3-methylpentane where necessary. Resonances were assigned for the three isomers of 3-methyl-2,4-dibromopentane as follows. *dl* pair: δ 1.03 (d, *J* = 7.5 Hz, 3 H), 1.71 (d, *J* = 7.5 Hz, 3 H), 1.77 (d, *J* = 7 Hz, 3 H), 1.9 (m, 1 H), 4.10 (d of q, *J* = 6.5 Hz, *J′* = 9 Hz, 1 H), 4.77 (q of d, *J* = 2.5 Hz, *J′* = 7 Hz, 1 H). *S-meso:* δ 1.15 (d, *J* = 6.5 Hz, 3 H), 1.67

---

(21) P. Lebeau and M. Picon, *C. R. Acad. Sci.*, **173**, 87 (1921).

(22) "Sadtler Standard Spectra," The Sadtler Research Laboratories, Philadelphia, Pa., 1969, IR No. 15315, 36954.

(23) C. S. Marvel and J. L. R. Williams, *J. Amer. Chem. Soc.*, **70**, 3842 (1948).

(24) P. Abelmann, *Chem. Ber.*, **43**, 1574 (1910).

(d, J = 7.5 Hz, 6 H), 2.27 (sextet, J = 7.5 Hz, 1 H), 4.35 (quintet, J = 6.5 Hz, 2 H). *R-meso:* δ 1.21 (d, J = 7 Hz, 3 H), 1.75 (d, J = 7 Hz, 6 H), 1.9 (m, 1 H), 4.19 (quintet, J = 6 Hz, 2 H).

Anal. Calcd for $C_6H_{12}Br_2$: C, 29.77; H, 4.98. Found: C, 29.83; H, 4.97 (for the mixture of three isomers formed by bromination of *trans*-(**1**)).

The residue, bp 61–63° (0.35 Torr), was identified as 2,3,4-tribromo-3-methylpentane, and accounted for ~10% of the isolated product: nmr δ 4.4 and 4.57 (q, 2 H), δ 1.85 (m, 9 H).

Anal. Calcd for $C_6H_{11}Br_3$: C, 22.33; H, 3.41. Found: C, 22.62; H, 3.49.

(b) **Bromine:Cyclopropane = 1:5 and 1:10.** The appropriate amount of bromine was added to the neat trans isomer under the conditions described above. With a fivefold excess of trimethylcyclopropane over bromine the secondary product was much diminished. At tenfold, it was no longer present, as determined by nmr. With the more reactive cis isomer, a slightly less than 2:1 excess of cyclopropane was sufficient to forestall secondary reaction. The recovered *cis*-**1** was shown to be unisomerized by vpc.

(c) **Bromination of *trans*-1,2,3-Trimethylcyclopropane at Reflux.** The neat trans isomer, 20 g, was refluxed on a steam bath and was illuminated by 400 W of incandescent light from a distance of 10 cm, and 3 g of bromine was added dropwise. The color was discharged immediately in an exothermic reaction, and large amounts of hydrogen bromide were formed. The products were distilled, and the fraction of bp <40° (1.3 Torr) was shown to be mainly 2-bromo-3-methylpentane by comparison of its nmr spectrum with that of an authentic sample, prepared by addition of hydrogen bromide to *trans*-**1**. A fraction of bp 47° (1.3 Torr) contained four major products as shown by vpc on column C at 130°. 3-Methyl-2,4-dibromopentane was identified by peak enhancement when co-injected with an authentic sample, and 3-methyl-1,2-dibromopentane was tentatively identified by nmr of a small sample collected by preparative vpc on column D: δ 0.85–1.05 (6 H), 1.25–1.6 (2 H), 1.75–2.1 (1 H), 3.55–3.95 (2 H), 4.2–4.7 (1 H). Collection problems precluded identification of other products.

(d) **Control Reaction. Dark.** A solution of 1.81 g of bromine and 1.0 g of the trans isomer in 12 ml of Spectrograde carbon tetrachloride was stored for 1 year in a foil-wrapped tube at 0–4° in a refrigerator. At the end of this time, a strong bromine color remained. The solution was washed with aqueous sodium thiosulfate rapidly and with brine, the solvent and the remaining cyclopropane were removed, and the residue was distilled to give only 0.8 g of material. Among the products, 3-methyl-2-bromopentane, 3-methyl-4-bromo-2-pentene, 3-methyl-2,4-dibromopentane, and two vicinal dibromides were tentatively identified by co-injection on column C at 130° with authentic samples. Three peaks remained unassigned in the vpc trace.

(e) **Control Reaction. Isoamyl Nitrite.** A solution of 2 g of *trans*-trimethylcyclopropane (0.0238 mol), 1.8 g of bromine (0.0124 mol), and 0.1 g of isoamyl nitrite (0.00114 mol) in 12 ml of carbon tetrachloride was stirred and cooled in an ice bath and was irradiated with two 300-W incandescent bulbs as above. After 2 hr, cooling was discontinued and the temperature rose to 55° in 3 hr under irradiation. After this time, a strong red color still persisted. The nature of the products was not investigated.

The isoamyl nitrite control was repeated on *cis*-**1**, and again bromine color remained after 5 hr. The solvent and excess reactants were removed under vacuum and the product was distilled to give 0.32 g of an oil. Glpc indicated that the dibromide product was >99% 3-methyl-2,4-dibromopentane, and nmr showed that the ratio of dibromide to 3-methyl-2,3,4-tribromopentane was 3:1. The ratio of *dl*:*S-meso* dibromide was 1.16:1.0; <1% of *R-meso* may have been present.

Reaction of 2,4-Dibromo-3-methylpentane with Bromine. A solution of 1.0 g (0.004 mol) of the title compound, prepared by the addition of bromine to *trans*-1,2,3-trimethylcyclopropane and distillation, and 0.5 g of bromine (0.0031 mol) in 25 ml of carbon tetrachloride was cooled to 0° and was irradiated under the same conditions as used in the bromination of the cyclopropane. Copious evolution of hydrogen bromide was observed, and the product, when excess starting material had been removed, gave the same spectrum as the tribromide obtained during bromination of **1** (*vide supra*).

Synthesis of 4-Bromo-3-methyl-2-pentene. Acid-catalyzed condensation of 2-butanone and acetaldehyde[25] served to synthesize 3-methyl-3-penten-2-one, which was reduced to the corresponding alcohol with sodium borohydride. The alcohol, 155 g, containing 3–4 drops of concentrated sulfuric acid, was stirred with a magnetic stirring bar, and hydrogen bromide gas was added. Periodically, the addition and the stirrer were stopped, and the aqueous lower layer was removed. Addition of hydrogen bromide was terminated when no more water was evolved, and the light tan product was washed with water and with brine. The product was then distilled through a 70-cm Vigreux column to give 175 g of the allylic bromide, bp 75° (63 Torr) (lit.[26] bp 62–64° (32 Torr)) and 8 g of 3-methyl-2,3-dibromopentane, bp 110° (63 Torr) (lit.[27] 72–74° (15 Torr), 48–50° (5 Torr)). This was used as "authentic" material where needed. The nmr of the latter compound was as follows: δ 1.06 (t, 3 H), 1.8 (m, 8 H), 4.42 (q, 1 H). The allylic bromide was a mixture of two isomers as shown by nmr: δ 1.8 (m, 9 H), 4.7 (q), 5.2 (q (together), 1 H), 5.4 (m, 1 H). By analogy to other allylic systems,[16] the predominant (10:1) isomer is the *cis*-allylic bromide based on the ratio of the areas of the quartets at δ 4.7:5.2.

Synthesis of 3-Methyl-2,4-dibromopentane *via* Free-Radical Addition of Hydrogen Bromide to 3-Methyl-4-bromo-2-pentene. A solution of 5 g of 3-methyl-4-bromo-2-pentene in 60 ml of hexane containing about 0.01 g of azobisisobutyronitrile was irradiated at 2537 Å in a quartz flask in a Griffin–Srinivasan photochemical reactor, and hydrogen bromide was bubbled in. The rate of addition was such that hydrogen bromide occasionally condensed on a Dry Ice filled cold finger condenser. After 70 min the addition was discontinued, and the reaction mixture was purged briefly with nitrogen. The solution was treated with sodium bicarbonate (solid) and was then washed with water and with brine, and dried over Drierite. Distillation gave a small amount of starting material, bp 49° (22 Torr), and then the desired dibromide, bp 71° (4.6 Torr) (lit.[9a] 83° (65 Torr)). The nmr indicated the presence of (*R*)-*meso*- and *dl*-3-methyl-2,4-dibromopentane accompanied by a small amount of the *S-meso* isomer.

Repetition of this reaction on a larger scale gave a mixture of 2,3- and 2,4-dibromides.

3-Methylpentane-2,4-diazide. A mixture of 20 g of sodium azide and 24 g of 3-methylpentane-2,4-diol ditosylate in 100 ml of HMPA or DMSO was stirred overnight under nitrogen. The mixture was then poured into 300 ml of water, the product was extracted with ether, and the ether was washed with water and brine, and was dried over Drierite. The solvent was removed, and the product was distilled to give 6.84 g of an oil, 72% of theoretical, bp 67–72° (3.2 Torr).

Anal. Calcd for $C_6H_{12}N_6$: C, 42.84; H, 7.20. Found: C, 43.43; H, 7.26.

An azide stretch was noted at 4.75 μ; nmr δ 0.9 (d, 3 H), 1.35 (m, 7 H), 3.6 (m, 2 H). This product was reduced to the diamine with $LiAlH_4$, and was then converted to the cyclic thiourea[28] by treatment with carbon disulfide.

Anal. Calcd for $C_7H_{14}N_2S$: C, 53.12; H, 8.92; N, 17.70. Found: C, 52.91; H, 8.81; N, 17.82.

***dl*- and (*S*)-*meso*-3-Methylpentane-2,4-diol.** A solution of 10 g (0.1 mol) of *cis*-3-methyl-3-penten-2-ol in 30 ml of tetrahydrofuran (THF) was mechanically stirred and was cooled in an ice bath. A solution of 0.8 *M* diborane in THF[29] (50 ml) was added. After 1 hr, sufficient water was added to quench excess diborane, and 90 ml of 3 *M* sodium hydroxide was added, followed by 50 ml of 30% hydrogen peroxide. (If the temperature was held at 0–10° during this time, the yield was lower than if the solution was permitted to warm spontaneously to 30–40°.) The solution was warmed to 55° and was stirred for 3 hr. When the solution was again cool, excess base was neutralized to a Bromthymol Blue end point with concentrated hydrochloric acid. Benzene and ether were stirred in, and the layers were then permitted to separate. The aqueous portion was removed and was extracted twice with chloroform. The combined organic solutions were concentrated, 10 g of glycerol and a trace of *p*-toluenesulfonic acid were added, and the diols were distilled to yield 6.8 g (58%), bp 95° (4.5 Torr).

***dl*- and (*S*)-*meso*-4,5,6-Trimethyl-1,3-dioxacyclohexane.** The mixture of diol isomers, 11.9 g, was mixed with 3.2 g of paraformaldehyde and 0.1 g of *p*-toluenesulfonic acid. The pressure was held at 50 Torr, and product was formed when the flask and contents were

---

(25) L. E. Hinkel, E. E. Ayling, J. F. J. Dippy, and T. H. Angel, *J. Chem. Soc.*, 814 (1931).

(26) A. Guillemonat, *Ann. Chim.* (*Paris*), **11**, 158 (1939).

(27) W. L. Evers, H. S. Rothrock, H. M. Woodburn, E. E. Stahly, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **55**, 1136 (1933).

(28) C. F. H. Allen, C. O. Edens, and J. VanAllan, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 394.

(29) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

heated to 90°. The products were trapped at −78° and were allowed to come to room temperature. Water was removed with a pipet, the dioxane was dissolved in ether, and the solution was dried with Drierite. Concentration and distillation gave 10.3 g (86% yield) of product, bp 148–154° at ambient pressure, 50–51° (18 Torr). The use of sulfuric acid as a catalyst led to yields in the vicinity of 50%. The two isomers were separated by vpc on column D at 170°. The earlier eluted was the *S-meso:* nmr δ 0.734 (d, J = 7 Hz, 3 H), 1.15 (d, J = 6 Hz, 7 H (obscures 1 H multiplet)), 3.16 (m, J = 6 Hz, J' = 8.5 Hz, 2 M), 4.48 (AB multiplet, 2 H).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.51; H, 10.74.

The next eluted was the *dl* pair: nmr δ 0.8 (d, J = 6.5 Hz, 3 H), 1.13 (d, J = 6.5 Hz, 3 H), 1.17 (d, J = 6.5 Hz, 3 H), 1.67 (m, 1 H), 3.57 (m, J = J' = 6.5 Hz, 1 H), 3.92 (m, J = 6.5 Hz, J' = 7.5 Hz, 1 H), 4.71 (AB multiplet, 2 H).

Anal. Found: C, 64.40; H, 10.77.

The *S-meso* compound was contaminated by 9% of *R-meso*, as estimated by nmr. The ratio of *dl*:*meso* was 1:1.12 by vpc (uncorrected).

***dl*- and (*R*)-*meso*-3-Methylpentane-2,4-diol.** The procedure reported above for the synthesis of *dl* and *S-meso* compounds was repeated on 10 g of *trans*-3-methyl-3-penten-2-ol to give the desired compounds.

***dl*- and (*R*)-*meso*-4,5,6-Trimethyl-1,3-dioxane.** The procedure reported for the synthesis of *dl* and *S-meso* dioxanes was repeated on a mixture of *dl*- and (*R*)-*meso*-3-methylpentane-2,4-diols. Vpc separation gave the *R-meso:* nmr δ 0.884 (d, J = 6 Hz, 3 H), 1.08 (d, J = 6.5 Hz, 7 H (obscures 1 H multiplet)), 3.67 (m, J = 6.5 Hz, J' = 2 Hz, 2 H), 4.74 (AB multiplet, 2 H).

Anal. Calcd: see above. Found: C, 64.60; H, 10.70.

This was contaminated by 15% of the *S-meso* dioxane as seen by nmr. The *dl* form then eluted, as described above. The ratio of *dl*:*meso* was 2.35:1 by vpc (uncorrected).

3-Methyl-2,4-diazidopentane (Reference Mixtures). In separate sequences, the diol mixtures described above were converted into the ditosylates. The crude ditosylates were then converted into the diazides by treatment with sodium azide in HMPA (*vide supra*). Each mixture of two diol isomers gave rise to a mixture of only two diazide isomers. This specificity permitted the following assignments of resonances (all except hydrogen on carbon 3). From the *S-meso* and *dl* diols; *dl* diazide: nmr δ 0.86 (d, J = 7 Hz, 3 H), 1.28 (d, J = 7 Hz, 3 H), 1.285 (d, J = 7 Hz, 3 H), 3.38 (m, J = 7 Hz, J' = 8 Hz, 1 H), 3.9 (m, J = 7 Hz, J' = 3 Hz, 1 H). *R-meso* diazide: nmr δ 0.986 (d, J = 7 Hz, 3 H), 1.32 (d, J = 6 Hz, 6 H), 3.52 (m, J = J' = 7 Hz, 2 H). From *R-meso* and *dl* diol; *dl* diazide as above, *S-meso* diazide: nmr δ 0.876 (d, J = 7 Hz, 3 H), 1.215 (d, J = 7 Hz, 6 H), 3.55 (m, J = J' = 7 Hz, 2 H).

Reaction of (*S*)-*meso*- and *dl*-3-Methyl-2,4-dibromopentane with Potassium Azide in Aqueous Acetone. A solution of 25 g (0.39 mol) of potassium azide and 5 g (0.0485 mol) of a 1:1 mixture of dibromide isomers (produced by radical bromination of *cis*-1,2,3-trimethylcyclopropane) in 125 ml of water and 500 ml of acetone was refluxed under nitrogen for 40 hr. Acetone was removed on a Roto-vap, the residue was added to water, and the products were extracted with pentane. Concentration and distillation gave 1 g (29%) of product which was largely diazide. The isomeric identification of the starting material was made by the observation of characteristic resonances for the *R-meso* diazide (δ 0.986, d, and 3.52, m), indicating the *S* configuration for the dibromide. This was accompanied by the *dl* diazide (δ 0.86, d; and 3.38 and 3.9, m) and unidentified impurities.

Control Reaction of (*R*)-, (*S*)-, and *dl*-3-Methyl-2,4-dibromopentane with Potassium Azide. The displacement described above was repeated exactly on the mixture of dibromide isomers produced by radical bromination of *trans*-1,2,3-trimethylcyclopropane. In this case, the predominant *meso* form was the *S-meso*, identified by characteristic resonances at δ 0.876 (d) and 3.55 (m). This was clearly accompanied by the *dl* pair, but the doublet for the *R-meso* (δ 0.986) was obscured by spinning side bands (max amount <20%).

Control Equilibration of Isomers of 3-Methyl-2,4-dibromopentane. A mixture of 5 g of dibromide from bromination of *trans*-trimethylcyclopropane, 20 g of sodium bromide, and 125 ml of HMPA was stirred for 52 hr under nitrogen at 25°. The suspension was then poured into 750 ml of water, and the dibromides were extracted with pentane. The organic solution was extracted with water and with brine, dried over Drierite, and distilled to give 1.0 g of dibromide, 20% recovery. The reaction was then repeated on 2.5 g of dibromide from bromination of *cis*-trimethylcyclopropane.

In the former case the original composition was *S*:*R*:*dl* = 1:0.55:1.53, and the final composition was 1:1.68:2.28. In the latter case, the starting composition was 1:(0):1.05; the final composition was 1:1.87:2.30.

Acknowledgments. This work was supported in part by National Science Foundation Grant GP-8372, and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund.

Photodimerization of Some Cyclopropenes

Charles D. DeBoer,* Donald H. Wadsworth, and William C. Perkins

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received July 19, 1972*

Abstract: The photochemistry of three 1,2-diphenylcyclopropenes (**1**, **2**, and **3**) has been studied. Direct irradiation gives no photodimers. Sensitized irradiation gives tricyclohexane dimers (major) and cyclopropylcyclopropenes (minor). The tricyclohexanes are thermally rearranged to 1,4-cyclohexadienes at widely varying temperatures. Quantum yield measurements and isotope effects show that the dimerization of **1** occurs in stepwise fashion with a diradical intermediate. Flash photolysis measurements show the triplet state of **1** is ≈60 kcal/mol. Nonvertical energy transfer to cyclopropenes appears to be unimportant. When low-energy sensitizers are used, the dimerization appears to include a termolecular step and can only be explained by a process similar to the Schenck mechanism.

The photodimerization of a cyclopropene was first studied by Stechl,[1] who found that the benzophenone-sensitized irradiation of 1,3,3-trimethylcyclopropene gives two isomeric dimers of tricyclohexane structure. Obata and Moritani[2] have also reported that both 3-acetyl- and 3-benzoyl-1,2-diphenylcyclopropene undergo dimerization to tricyclohexanes upon irradiation, undoubtedly by intramolecular sensitiza-

---

(1) H. H. Stechl, *Chem. Ber.*, 97, 2681 (1964).

(2) N. Obata and I. Moritani, *Tetrahedron Lett.*, 1503 (1966).