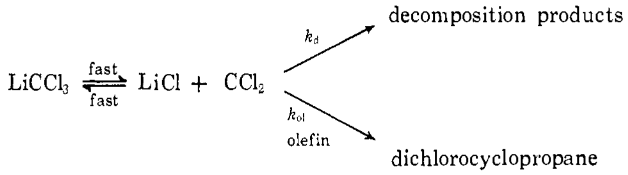
of olefins, the precipitate dissolved accompanied by a dramatic temperature increase and the formation of a dark polymer. In the presence of olefins the decomposition was accelerated and good yields of the corresponding dichlorocyclopropanes were obtained. They proposed that CCl_2 was not the cyclopropanating reagent, arguing that olefins should not accelerate its formation. Although these authors[14,15] favor the direct reaction of $LiCCl_3$ with olefin, this mechanism is not imperative. Three considerations weaken their conclusion.

(1) The observation that in the presence of olefin $LiCCl_3$ is consumed more rapidly than in the absence is also consistent with a fast reversible formation of CCl_2 from $LiCCl_3$ as follows.

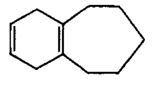


In the absence of olefin the rate of decomposition is determined by k_d; dichlorocyclopropane formation adds to this rate. This explanation is similar to that of Seyferth[21] for $PhHgCCl_2Br$ thermolyses. (2) The electrophilicity of the reagent is not consonant with the carbanion formulation, MCX_3. (3) The competition data in Table I show $LiCCl_3$–olefin reactivities plot on the same Arrhenius line as those for free CCl_2.

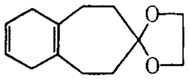
There remains no substantive evidence for an intermediate other than free CCl_2 in dichlorocyclopropanation of olefins, regardless of source. Dichlorocarbene complexed to solvent or other nucleophilic species is not sufficiently reactive in transfer of CCl_2 to olefins; $LiCHCl_2$ and MCH_2X do transfer directly to olefins the fragments CHCl and CH_2, respectively. Of course it does not follow that MCX_3 is incapable of participating in a direct transfer of CX_2 to some as yet unstudied substrate.[22]

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research.

[22] Vogel[23] has observed that CCl_2 from $CHCl_3$ + base adds to each of the double bonds in



at about the same rate. In contrast, CCl_2 addition to the internal double bond in



occurs three times faster than to the peripheral double bond. This enhanced reactivity can be ascribed to initial formation of a carbene–oxygen complex followed by an intramolecular CCl_2 transfer to the nearer double bond.

[23] E. Vogel, private communication.

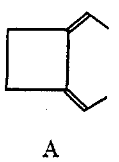
The Stereochemistry of Allene Dimerization[1]

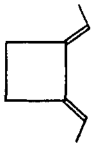
Thomas L. Jacobs, John R. McClenon, and Oliver J. Muscio, Jr.

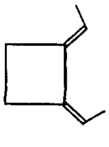
Contribution No. 2390 from the Department of Chemistry, University of California, Los Angeles, California 90024.
Received May 20, 1969

Abstract: The main dimer of chloroallene has been shown to have the structure and stereochemistry shown in IXa. The main dimer of 1-chloro-3-methyl-1,2-butadiene has structure IV, but the stereochemistry of the ring chlorines remains in doubt. Ozonization of IV gave *dl*-α,α'-dichlorosuccinic acid, but the dipole moment (2.63 D) does not agree with values calculated for *cis* (3.50 D) or *trans* (1.44 D) isomers. The mechanism of allene dimerizations is discussed.

Allene dimerization which results in the formation of substituted 1,2-dimethylenecyclobutanes has been known and studied for more than 50 years, but, until recently, little was known of the stereochemistry of this reaction. Vicinal substituents on the cyclobutane ring may lie either *cis* or *trans* to each other, and those on the exocyclic double bonds may face either inward toward each other (A), outward (B), or be unsymmetrically arranged (C).


A


B


C

Some recent work has indicated that halogen cyclobutyl substituents may be *trans* to each other. Ozonolysis of I, the major dimer of 1-bromo-3-methyl-1,2-butadiene,[2] and of II, the dimer of tribromoallene,[3] yielded *dl*-α,α'-dibromosuccinic acid, which was taken as proof of *trans*-bromines in these dimers; the nmr spectrum of the dimer mixture from trichloroallene[4] was interpreted as suggesting that the chlorines were *trans* in the major isomer, assigned structure III.

---

[1] This research was supported by Grants GP-5530 and GP-8489 from the National Science Foundation, and by earlier grants from the National Science Foundation and from the U. S. Army Research Office (Durham). Many of the results are taken from the Ph.D. Thesis of John R. McClenon, University of California, Los Angeles, 1964.

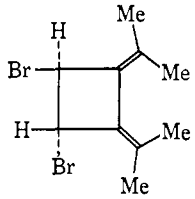
[2] T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1361 (1963).

[3] A. Roedig and N. Detzer, *Liebigs Ann. Chem.*, **710**, 1 (1967).

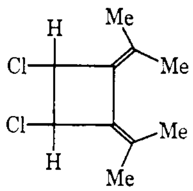
[4] A. Roedig and N. Detzer, *Angew. Chem.*, **80**, 482 (1968).

On the other hand, ozonolysis of the major dimer of 1-chloro-3-methyl-1,2-butadiene has been reported[5] to yield a mixture of *meso*- and *dl*-α,α'-dichlorosuccinic acid, suggesting the possibility of *cis* structure IV, with partial isomerization during ozonolysis. Ozonolysis of V, the dimer obtained from 1,3-diphenylallene, gave[6] *meso*-α,α'-diphenylsuccinic anhydride, proving *cis* substitution. A dipole moment measurement of the major dimer, VI, of 1,1-diphenyl-3-chloroallene showed that dimer to have *cis* chlorines.[7]

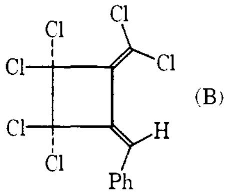
Less data have appeared concerning stereochemistry at the exocyclic methylenes. In the case of V, and in that of the cross-dimer VII of 1,3-diphenylallene and perchloroallene,[8] it has been assumed that the larger group will take the outward, presumably less crowded position (B). However, in one case, such a substituent has been reported[9] at the inward side (A) of the double bonds in the minor dimer VIII of 1-chloro-3-methyl-1,2-butadiene.



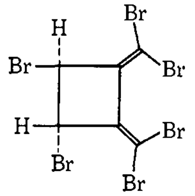
I



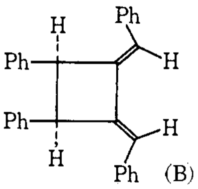
IV



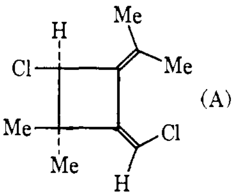
VII



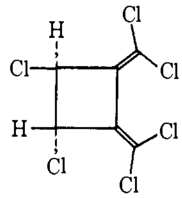
II



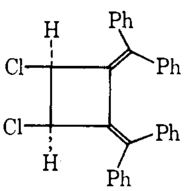
V



VIII



III



VI

Thus, on the basis of currently published reports, there appears to be no clear trend in the stereochemistry of allene dimerization, except that the more highly substituted or conjugated allenyl carbon usually appears at the exocyclic position in the dimer, giving the thermodynamically most stable product.[10]

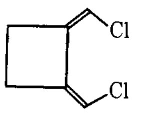
It was with the hope of gaining further insight into the stereochemistry and mechanism of this reaction that we undertook a study of the dimerization of 1-chloroallenes.

Results

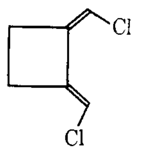
Chloroallene. Dimerization of chloroallene at 60° resulted in a product distribution, following removal of unreacted allene, of 20–25% dimer, 25–30% trimer, 35–40% tetramer, and 0–5% higher polymers. The dimeric fraction was separated by fractional distillation, and the isomers were isolated by preparative gas chromatography.

A gas chromatogram of the dimer mixture on an early instrument indicated that the major isomer represented about 80% of the dimers, but examination of an nmr spectrum suggests it might be as high as 90%. This dimer has two signals in its nmr spectrum, at τ 4.30 and 7.38, with areas in the ratio 1:2, respectively. The ultraviolet spectrum of this dimer has a peak at 258 mμ, with shoulders at 248 and 268 mμ; the uv spectrum of 1,2-dimethylenecyclobutane contains a peak at 246 mμ, with shoulders at 238 and 255 mμ, while 1,3-dimethylenecyclobutane has no absorption maxima between 350 and 220 mμ. These spectral data are consistent only with a 1,2-dimethylenecyclobutane structure with the chlorines on the double bonds, not on the ring. This conclusion is confirmed by the results of ozonolysis of the dimer; the product so obtained is succinic acid, as expected.

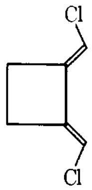
Three isomeric structures are possible, but IXb may be eliminated because of the symmetry of the nmr spectrum.



IXa



IXb



IXc

The nmr spectrum of 1,2-dimethylenecyclobutane contains two vinyl proton signals at τ 5.42 and 4.98 in the ratio 1:1. The inner protons should be deshielded both by "bumping,"[11] and by the diamagnetic anisotropy of the opposing double bond, so their signal must appear downfield at τ 4.98, while the outer, undisturbed protons resonate at τ 5.42.

Since chlorine substitution causes a downfield shift of 0.95–1.05 ppm[12] in vinyl chloride and several similar compounds, the vinyl protons in the chloroallene dimer should resonate about 1.0 ppm downfield from those in 1,2-dimethylenecyclobutane, at τ 4.4 and 4.0 for outer and inner protons, respectively. The peak in the actual spectrum occurs at τ 4.3; the protons are probably outward, and the chlorines inward as in IXa.

This assignment is confirmed by the dipole moment of the dimer, for which the measured value is 3.0 ± 1.0 D. The expected value for IXc would be 0.75 D, well outside the experimental limits of error, while the expected value for IXa is 3.0 D.

The two minor dimers (<10%) of the mixture were not completely separated from each other in sufficient quantity for nmr analysis, but a nmr spectrum of a mixture of the two suggests that the predominant one may have the structure X. The uv spectrum is similar to that of the major dimer.

1-Chloro-3-methyl-1,2-butadiene. In a study of the dimerization of 1-chloro-3-methyl-1,2-butadiene parallel to that of Bertrand,[5,9] we have found dimers IV and VIII to be present in the ratio of 9:1 by gas

---

(5) M. Bertrand, H. Reggio, and G. Leandri, *C. R. Acad. Sci., Paris, C*, **259**, 827 (1964).

(6) E. V. Dehmlow, *Chem. Ber.*, **100**, 3260 (1967).

(7) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 2707 (1963).

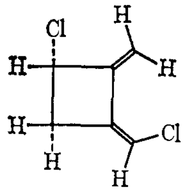
(8) E. V. Dehmlow, *Chem. Ber.*, **100**, 3260 (1967).

(9) M. Bertrand and R. Maurin, *C. R. Acad. Sci., Paris, C*, **265**, 609 (1967).

(10) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

(11) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).

(12) (a) C. N. Banwell and W. Sheppard, *Mol. Phys.*, **3**, 351 (1960); (b) E. B. Whipple, *et al.*, *J. Chem. Phys.*, **34**, 2136 (1961).



X

chromatographic analysis; however, we have always isolated only *dl*-α,α'-dichlorosuccinic acid upon ozonolysis of IV. Apparently, our procedure must differ from that used in Bertrand's laboratories, which has not been reported. Since under our conditions, we have also obtained this *dl* acid upon ozonolysis of VI, shown to have *cis* chlorines by dipole moment measurement,[7] we undertook a careful dipole moment measurement of IV in benzene solution; the method of Halverstadt and Kumler[13] was used for evaluation.

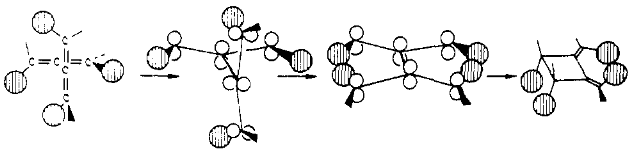
The dipole moment value so obtained is $\mu = 2.63 \pm 0.01$ D; the expected value for a *cis* planar geometry, based on an estimated C–Cl bond dipole moment of 1.90 D[13] in benzene, is $\mu = 3.50$ D, while that for a *trans* planar geometry would be 1.44 D. In order to fit theoretical expectations to the observed value, it is necessary to assume a ring puckering of about 60° for both *cis* and *trans* cases, an assumption unreasonable for cyclobutane systems.

Discussion

The dipole moment of IV does not help distinguish between structures with *cis* and *trans* geometry for the ring chlorines, and the evidence from degradation by ozonization is equally ambiguous. It is not possible to rule out rearrangement during the ozonization because intermediates having a keto group α to a halogenated carbon are quite possible during the degradation, and enolization would then permit equilibration. The simplest explanation for the observed dipole moment is that the *cis* and *trans* isomers of IV have formed a 1:1 complex or that a eutectic crystallized out. However glpc did not show any separation of the crystalline material into components, and the 100-MHz nmr spectrum of IV shows only a single peak for the cyclobutyl protons; some difference in chemical shift would be expected between *cis* and *trans* protons. The observation by Bertrand and coworkers[5] that ozonization gives a mixture of *meso*- and *dl*-α,α'-dichlorosuccinic acid also suggests that IV may be a mixture. Further work will be done on the major dimer of 1-chloro-3-methyl-1,2-butadiene.

The finding that the vinyl chlorides in IXa are pointing inward gives additional weight to the report of Bertrand[9] that the vinyl chlorine of VIII is oriented inward, contrary to what one would expect on the basis of least crowding. In a previous communication[14] on dimers of 1-chloro-3-mesitylallene we have shown that mesityl groups, which are still larger, may occupy the more crowded inward positions in the exocyclic double bonds. There is evidence that this orientative preference extends to the methyl group as well.[15]

It was suggested some time ago[10] that the products of thermal dimerization of allenes could be accounted for by formation of a biradical through union of the central carbons of allenyl systems and subsequent ring closure. Recently,[16] evidence was presented that allene itself may dimerize by this mechanism. The stereochemistry observed at the exocyclic methylenes can be rationalized by postulating initial formation of an orthogonal biradical, XI, in which orientation of the larger substituents at both ends of each allyl moiety is determined by the steric requirements of that group. Examination of models suggests that the inward positions, represented by the shaded circles in XI, are somewhat less crowded than the outward. The most stable configuration would then be represented by XI with the positions of the largest groups shown by the shaded circles. Closure of the biradical would then place the exocyclic substituents in the inward orientation observed.



XI XII XIII

In our earlier communication,[14] we suggested that the closure of the biradical might be disrotatory, giving *cis*-cyclobutyl substituents, a suggestion based on the molecular orbital symmetry of the planar biradical. This is shown in XII and XIII. Consideration of the orthogonal biradical molecular orbitals indicates that the closure could be conrotatory, a conclusion appearing to be in better agreement with experimental observation of *trans* isomers. It would seem that closure is either nonstereospecific, with the ratio of *trans* to *cis* isomers determined by their relative stabilities, or is conrotatory, with the ratio determined by the relative populations of inward- and outward-substituted allylic biradicals. It is at present not possible to distinguish between these two possibilities, although in one case[15] it has been demonstrated that ring opening to a biradical may be conrotatory.

It is not easy to explain our stereochemical results by a concerted mechanism because the steric crowding found in the final products should destabilize the transition states leading to them.[17]

---

(13) J. W. Smith, "Electric Dipole Moments," Butterworth and Co., Ltd., London, 1955.

(14) O. J. Muscio, Jr. and T. L. Jacobs, *Tetrahedron Letters*, 2867 (1969).

(15) The dimers of methylallene and their thermal isomerization have been examined by J. J. Gajewski, who has found a strong tendency for the exocyclic methyls to take the inward orientation we have observed for chloro and mesityl substituents. The stereochemistry of the thermal isomerization of the dimers suggests a conrotatory opening of the cyclobutane ring. We wish to thank Dr. Gajewski for making copies of his papers (submitted for publication) available to us before publication.

(16) W. Von E. Doering and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **89**, 4534 (1967).

(17) Since this manuscript was submitted we have learned of work at MIT under the direction of Professor W. R. Moore on the dimerization of 1,2-cyclononadiene. This work, published in the Ph.D. thesis of T. M. Ozretich, describes the thermal dimerization of optically active and racemic 1,2-cyclononadiene. Results are in accord either with a concerted mechanism or a biradical mechanism in which the biradical is formed by joining two allenes through the central carbons with conrotatory or disrotatory turning of the groups at one end of each allenyl moiety to form the allylic parts followed by flattening of the biradical and ring closure in the opposite sense to give the cyclobutane ring. It appears to us that two 1,2-cyclononadiene molecules might give a biradical in which the three carbons involved in the allylic system in each ring might not readily be planar and the biradical would then be much less stable. A concerted mechanism could then be the preferred course of the reaction.

Experimental Section

Melting points are corrected. Ultraviolet spectra were recorded on a Cary Model 14 spectrometer; nuclear magnetic resonance spectra were recorded on a Varian A60 instrument in carbon tetrachloride solution with internal tetramethylsilane as reference. Molecular weight determinations were made with a vapor pressure osmometer made by Mechrolab, Inc. Refractive indexes were determined with an Abbe-type Spencer refractometer.

A. **Chloroallene.** Propargyl chloride (450 g) and 1 lb of sodium hydroxide pellets were shaken together at ambient temperature for 3 days. The propargyl chloride was obtained from Antara Chemicals Co.[18] and used without further purification. Its purity was bettter than 99% by vpc.

Equilibrium was reached at 89% chloroallene–11% propargyl chloride. The contents of the flask were vacuum transferred, dried, and fractionally distilled. Chloroallene was obtained in a yield of 74–78%, bp 44.5°, 99.9% pure by gas chromatography.

Dimerization. Chloroallene (20 g) and 0.5 g of hydroquinone were heated at 60° for 3 or 4 days, and the volatile material was taken off under vacuum. Polymer was removed from the residue by treatment with 20–30 volumes of methanol, filtration, and evaporation of solvent, followed by similar treatment with petroleum ether (Skellysolve B, bp 60–70°). The dimeric material was separated from the higher oligomers by vacuum distillation, bp 35–55° (1 mm). A molecular weight determination by vapor phase osmometry gave a value of 148 (calculated for dimer, 149).

The major isomer, IXa, was isolated by preparative gas chromatography at 120° on a GE-30 column. The minor isomers were unstable, and no more than a few milligrams of each was isolated.

Anal. Calcd for $C_6H_6Cl_2$ (major dimer): C, 48.36; H, 4.06. Found: C, 48.46; H, 4.20.

Ozonolysis of IXa. IXa (0.5 g) was dissolved in 10 ml of chloroform and cooled to −10°. Ozone was passed through the solution at a rate of 0.112 mequiv/min for 90 min. The resulting solution was allowed to warm to room temperature and treated with 10 ml of 10% hydrogen peroxide. Removal of solvent gave 0.3 g of a white crystalline solid, mp 189–190°, after recrystallization from ether–benzene. Authentic succinic acid recrystallized in the same manner melted at 190–190.5°. The mixture melting point was not depressed, mp 189.5–190.5°

Dipole Moment of IXa.[19] Six solutions of IXa in carbon tetrachloride were prepared over a concentration range of 4.6–0.4 mole %; measurements of dielectric constant at 25° were made for the six solutions and for pure solvent. A linear relationship between refractive indexes and concentration (in mole per cent) of the solutions was observed and the dipole moment was calculated by Smith's method.[13]

B. **1-Chloro-3-methyl-1,2-butadiene.** This allene was prepared by the method of Hennion;[20] methylbutynol was obtained from Air Reduction Co.[18]

Dimerization. 1-Chloro-3-methyl-1,2-butadiene (75 g), 0.5 g of anhydrous potassium carbonate, and 0.1 g of hydroquinone were heated at 80–90° for 13 days. The volatile fraction was removed under vacuum, and the residue distilled (59.5 g), bp 70–76° (0.35 mm). The distillate was diluted with an equal volume of acetone; the resulting solution was stored overnight at −20° and chilled briefly in Dry Ice; the resulting crystals of IV were collected, recrystallized from 30 ml of acetone, and dried *in vacuo* at room temperature: yield 22.0 g (29% of theory); mp 60.0–60.6°. The melting point was unaffected by sublimation of the recrystallized dimer, which was unstable upon overnight exposure to air at room temperature, and was stored at −20°: nmr τ 8.18 (6), 8.02 (6), 5.44 (2); uv λ_{max} 273 mμ (ϵ 13,600).

Anal. Calcd for $C_{10}H_{14}Cl_2$: C, 58.56; H, 6.88. Found: C, 58.31; H, 7.13.

Gas chromatographic analysis of the original mixture showed that two dimers were present in the ratio 9:1. The minor component was isolated by preparative gas chromatography.

Ozonolysis of IV. Dimer (0.5 g) was dissolved in 10 ml of carbon tetrachloride and treated with a large excess of ozone. The resulting solution was treated with hydrogen peroxide as before, and the solvent removed. (The remaining solid (100 mg) melted at 175–176° and was found to be identical with authentic *dl*-α,α'-dichlorosuccinic acid, mp 174.5–176°, mmp 174.5–175.5°). Unreacted dimer (150 mg) was recovered. Essentially the same result was obtained when ozonolysis was carried out in ethyl acetate at −50°.

Dipole Moment of IV. Solutions of IV in benzene were prepared under a water and oxygen-free nitrogen atmosphere, using benzene which had been dried by refluxing over sodium and fractionally distilled under dry nitrogen. The dimer was weighed out into glass-stoppered flasks, which were then stored under the inert atmosphere, where each solution was prepared just prior to its dielectric constant determination.

A series of six solutions were prepared with a range of weight fractions of 0.0024218–0.019247, and were used for dielectric constants and specific volume determinations. .In order to extend the range of index of refractions to a useful degree, these, and two other solutions up to a weight fraction of 0.036068, were used in that determination. All measurements were made in a bath thermostated at 25.00°. The dielectric constant, specific volumes, and squares of the index of refraction of these solutions varied linearly with the weight fraction of IV in the range examined. The slopes of these three functions, and their standard deviations, were calculated by the method of least squares.[21]

---

(18) We wish to thank Antara Chemicals Co., for a gift of generous amounts of propargyl chloride and Air Reduction Co. for a gift of generous amounts of methylbutynol.

(19) We are grateful for the assistance of Jack Wilt, who made the dielectric constant measurements.

(20) G. F. Hennion and A. P. Boiselle, *J. Org. Chem.*, **26,** 725 (1961).

(21) NOTE ADDED IN PROOF. The structure of VI, previously reported to have *cis* chlorines,[7] has been reexamined by E. V. Dehmlow and assigned a *trans* structure on the basis of redetermination of the dipole moment and isolation of *dl*-dichlorosuccinic acid from ozonization. We have also isolated this acid as the only pure product from ozonization of this dimer. Dehmlow has also found that the major dimer from 1-bromo-3,3-diphenylallene has *trans* ring bromines and that the *cis* dimer of 1,3-diphenylallene is accompanied by the *trans* isomer (about equal amounts). On the basis of this work it seems probable that 1-halo-3,3-disubstituted allenes usually yield the dimer having *trans* ring halogens as the major product and that the corresponding *cis* isomer is not formed. 1-Chloro-3-methyl-1,2-butadiene may be anomalous, however. We wish to thank Dr. Dehmlow for making a copy of his paper (submitted to *Tetrahedron Letters*) available to us before publication.