

Chemistry of *gem*-Dihalocyclopropanes. IX. The Stereospecific Synthesis of Conjugated *meso*-Diallenes

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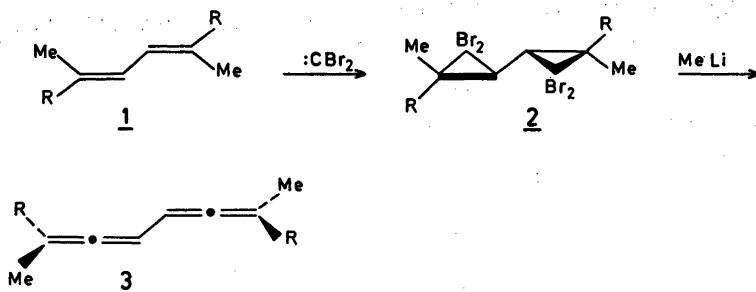
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Addition of dibromocarbene to the conjugated *E,E*-dienes **1b** and **1c** occurred stereoselectively in two cases to give the corresponding bis-adducts **2b** and **2c** with *meso*-configuration. Treatment of the bis-adducts with methyllithium proceeded with stereospecific ring-opening to the corresponding *meso*-diallenes **3b** and **3c**. The stereoselectivity of the addition reaction is rationalized by discussing the possible conformations of the intermediate vinyl-dibromocyclopropane derivatives. The second reaction is explained in terms of a preferred mode of ring-opening of a cyclopropylidene-like intermediate.

Diallenes represent a unique diene system, and they have been shown to undergo interesting intramolecular^{1,2} and intermolecular^{3,4} thermal reactions. In order to study the stereochemistry of these reactions it is necessary to use a chiral diallene of known configuration. A synthesis of diallenes which has some general applicability involves the addition of dibromocarbene to a diene followed by reaction of the bis-adduct with methyllithium; cyclic^{3,5,6} and noncyclic diallenes^{3,7} have been prepared by this method. The present work describes the stereospecific synthesis of conjugated *meso* diallenes by this

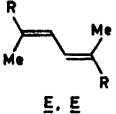
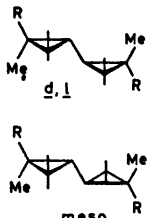
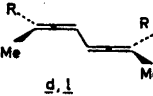
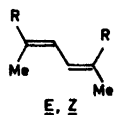
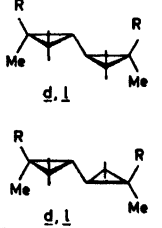
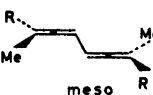
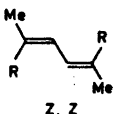
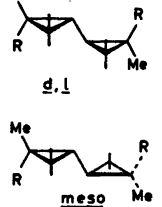

twostep reaction sequence⁸ (Scheme 1).

The addition of dibromocarbene to 2,5-dimethyl-2,4-hexadiene (**1a**) exhibited some stereoselectivity in that *meso* and racemic bis-adducts **2a** were formed in a ratio of 2.3:1;⁹ both reacted with methyllithium to give exclusively 2,7-dimethyl-2,3,5,6-octatetraene (**3a**), a non-chiral diallene. However, by replacing one methyl group at each end of the diene **1a** with another substituent three possible stereoisomeric dienes could result and the addition of dibromocarbene could lead to six different bis-adducts as shown in Table 1. Each of these bis-adducts could react with methyllithium to *meso*- and racemic diallenes. It was therefore essential to use one of the geometric isomers of **1** as starting material and preferably the *E,E*- or *Z,Z*-isomer because if necessary the separation of *meso*- and racemic forms of the bis-adduct was expected to be easier than that of two racemates. Recently, the cuprous salt-catalyzed coupling of vinylic lithium¹⁰ or Grignard¹¹ derivatives have been shown to yield the corresponding conjugated dienes with a high degree of stereospecificity, and this procedure was attempted for the preparation of the *E,E*-isomers of **1**.



Scheme 1.

Table 1.

Diene	Diastereomeric	
	Bis-adducts	Diallenes
 E, E	 d, l meso	 d, l
 E, Z	 d, l meso	 meso
 Z, Z	 d, l meso	 meso

The lithium derivative from *E*-1-bromo-2,3,3-trimethyl-1-butene¹² was successfully coupled in 87% yield to the diene-2,2,3,6,7,7-hexamethyl-3*E*,5*E*-octadiene (*Ib*). Coupling of the Grignard derivative of *E*-1-bromo-2-phenyl-1-propene¹³ in tetrahydrofuran gave a 48% yield of crystalline 2,5-diphenyl-2*E*,4*E*-hexadiene (*Ic*)¹⁴ besides some α -methylstyrene and 1-phenyl-1-propyne; the lithium derivative of the above bromide could not be used because it rearranges rapidly to an equilibrium mixture of *E*- and *Z*-1-lithio-2-phenyl-1-butene and 1-phenyl-1-propyne.¹⁵ On the other hand, we were not able to obtain pure *E*-1-bromo-2-methyl-1-butene, the starting material for the preparation of 3,6-dimethyl-3*E*,5*E*-octadiene (*Id*); consequently, the diene was prepared by a conventional synthetic route.

Reaction of 1-bromo-3-methyl-2-pentene and triphenyl phosphine afforded the phosphonium salt, and the corresponding ylid reacted with

Table 2. Tetrabromobicyclopropyl derivative (2) from dienes (1) and dibromocarbene.

Diene 1 R	Diadduct 2		Yield %
	Racem. %	meso %	
<i>a</i> Me	30	70	92
<i>b</i> <i>t</i> -Bu	0	100	27
<i>c</i> Ph	0	100	44
<i>d</i> Et ^a			75 ^b

^a Mixture of geometric isomers. ^b Complex mixture of diastereomers.

2-butanone to yield the diene *Id* as a mixture of 50% *E,E*-, 40% *E,Z*-, and 10% *Z,Z*-isomers. These could unfortunately not be separated by fractional distillation.

The addition of dibromocarbene, generated from bromoform and potassium *t*-butoxide, to the dienes gave the corresponding bis-adducts in varying yields (Table 2). The structures were assigned on the basis of spectral data. It is worth noting that the mass spectral data provide little information; in no case was the molecular ion observed and usually the highest observable mass was a result of extensive fragmentation. Both products *2a* and *2d* were stereoisomeric mixtures, but on the other hand compounds *2b* and *2c* were homogeneous as shown by thin layer chromatography. Their configurations were established by crystallographic measurements; space group determinations demanded that both molecules have a centre of symmetry, a requirement which is only satisfied by the *meso*-form. Hence, a highly selective addition of the carbene had taken place. Unfortunately, the yields of these bis-adducts were not good; compound *2c* was accompanied by some unreacted starting material

Table 3. Conjugated diallenes (3) from tetrabromobicyclopropyl derivatives (2) and methyl-lithium.

Bis-adduct 2	Diallene 3	Yield %
<i>a</i>	[Me ₂ C=C=CH-] ₂	93 ^a
<i>b</i>	[<i>t</i> -Bu(Me)C=C=CH-] ₂	91
<i>c</i>	[Ph(Me)C=C=CH-] ₂	90
<i>d</i>	[Et(Me)C=C=CH-] ₂	82

while from the reaction of *1b* a liquid was actually obtained as the major product. It consisted mainly of two isomeric bromides in a ratio of approximately 4:1, but decomposition on attempted separation by preparative gas chromatography has hampered the structural elucidation; further work is in progress and will be reported in due course. The product from the addition of dibromocarbene to the diene *1d* consisted of a mixture of stereoisomeric bis-adducts, as expected, since the diene was stereochemically heterogeneous.

Treatment of the bis-adducts with methyl-lithium afforded in each case the corresponding diallene in high yield (Table 3). From both *meso-2b* and *meso-2c* single products were obtained as indicated by the NMR spectra and the configurations were shown in both cases to be *meso* since the crystallographic space group demanded a centre of symmetry.

A complete X-ray analysis of the diallene *3c*¹⁵ confirmed this conclusion. The conversion of the dibromocyclopropane ring to the corresponding allenic linkage had occurred with complete stereospecificity. As expected, the diallene *3d* obtained from the mixture of bis-adducts *2d* consisted of a mixture of stereoisomers as indicated by the NMR spectrum, but all attempts to separate them were unsuccessful.

DISCUSSION

Addition of dibromocarbene to symmetrically substituted conjugated *E,E*-dienes can only lead to a single vinylcyclopropane derivative independent of which double bond reacts; however, the vinylcyclopropane derivative can react further with a second mole of carbene to give either *meso* or racemic bis-adduct depending on the direction of addition to the double bond. This has been verified experimentally; 1,3-butadiene and dichlorocarbene afforded a mixture of almost equal amounts of the two stereoisomeric bis-adducts;¹⁶ dibromocarbene and 2,5-dimethyl-2,4-hexadiene yielded a mixture consisting of 70% *meso* and 30% racemic bis-adducts, whereas from 2,3-dimethyl-1,3-butadiene the *meso*-bis-adduct was obtained exclusively.⁹ Cyclic conjugated dienes add dihalocarbenes preferentially *anti* with formation of racemic bis-adducts.^{16,17} This selectivity must

essentially result from steric factors which would also be expected to determine the selectivity in additions to the dienes *1* of the present work. Consequently, knowledge about possible conformations of the intermediate vinylcyclopropane derivatives could provide an explanation for the preferred formation of *meso* bis-adducts.

In the gas phase vinylcyclopropane itself exists as an equilibrium mixture of approximately 75% *anti* and 25% *gauche* conformations with a free energy difference at 20 °C of about 1 kcal/mol.¹⁸ NMR spectroscopy indicates that such an equilibrium is also present in solution.^{19,20} However, a similar study on 1-isopropenyl-1-methylcyclopropane indicates that the *anti* conformation does not contribute significantly to the rotational equilibrium; steric repulsion between the cyclopropyl methyl group and the vinylic hydrogen, estimated to about 1–1.5 kcal/mol, is sufficient to shift the equilibrium towards a *gauche* conformation.²¹ For 1,1-dibromo-2-vinylcyclopropane NMR studies indicate a preferred conformation in which the double bond is rotated about 90° from the *anti* position owing to hydrogen-bromine repulsion.²⁰ Molecular models suggest that both the hydrogen-methyl and the hydrogen-bromine interactions described above would be

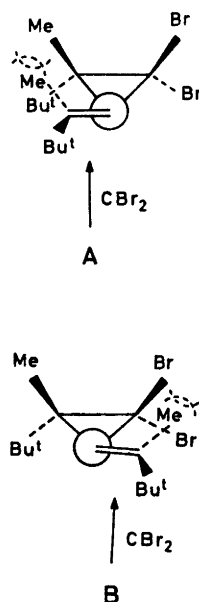


Fig. 1.

important in the *anti* conformation of the vinyl-cyclopropane precursors of the bis-adducts **2b** and **2c**. We therefore assume that these compounds will prefer a *gauche* conformation as depicted in Fig. 1 for the case of adduct **2b**. The double bond can rotate clockwise or counter-clockwise. The former mode will first encounter van der Waals contact between the methyl and *t*-butyl groups and having passed this barrier serious methyl-methyl interactions are apparent after about 70–80° of rotation (Fig. 1, A). The latter mode will result in van der Waals contact between a bromine atom and a methyl group after about 70–80° (Fig. 1, B). It seems reasonable that the conformer B will be of lower energy, an assumption which is also supported by the observed conformational equilibrium of 2-bromobutane in which a methyl-bromine interaction is preferred over a corresponding methyl-methyl interaction.²² A similar argument can be presented for adduct **2c**. The least hindered approach to the double bond of conformer B would be from the bottom phase, and consequently the addition of dibromocarbene would be expected to yield the *meso* bis-adduct. The same approach is also the least hindered one in the case of conformer A, but in this case the racemic bis-adduct would result.

Extensive experimental results indicate that reactions of *gem*-dibromocyclopropane derivatives with methyllithium lead to a carbene-like intermediate which subsequently can undergo ring-opening²³ to an allene. The geometry of the allene demands that this ring-opening is conrotatory²⁴ or monorotatory.²⁵ Substituted cyclopropylidenes with an *E*-configuration will have two distinctly different modes of ring-opening, *a* and *b*: (Fig. 2).

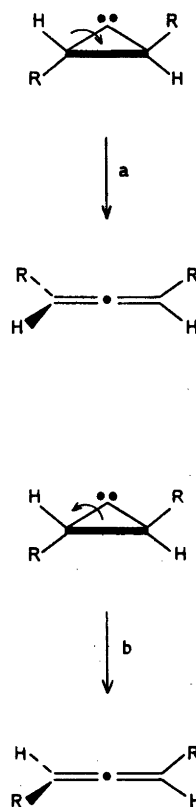
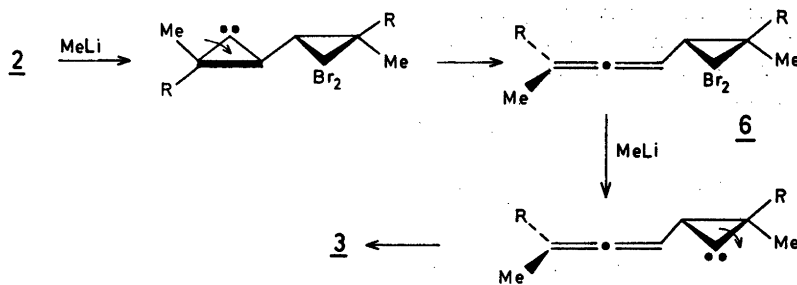


Fig. 2.

Mode *a* creates the least steric interaction during the bond rotations because the substituents R and R' are moving away from each other, and experiments^{24,25} have shown that this is indeed the preferred mode. Applying this knowledge to our present system provides an explanation for the observed stereospecificity



Scheme 2.

R = Bu^t or Ph

of the bis-adduct to diallene conversion; *meso* bis-adduct **2** is converted *via* the allene **6** to *meso* diallene **3** by employing twice the *a* mode of ring-opening as shown in Scheme 2. Preference for mode *a* can probably only be important if the steric bulk of group R is considerably larger than that of a methyl group. The stereochemistry of the ring-opening to diallenes of other bis-adducts is under study.

EXPERIMENTAL

NMR spectra were recorded on Varian Associates A60A and HA100-15D spectrometers. Mass spectral data were obtained using an A.E.I. MS 902 mass spectrometer. A Perkin-Elmer model 457 spectrophotometer was used for obtaining IR spectra, and UV spectra were recorded on a Cary 14 spectrophotometer. Gas chromatographic analyses were performed with Varian Aerograph Models 90P and 711. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, West Germany. All reactions were carried out under pure nitrogen.

E,E-2,2,3,6,7,7-Hexamethyl-3,5-octadiene (1b)
A solution of 18.0 g (0.1 mol) of *E*-1-bromo-2,3,3-trimethyl-1-butene¹² in 25 ml of dry ether was added to 2.0 g (0.28 g at.) of lithium in 75 ml of dry ether with vigorous stirring and cooling (ice). After 3 h stirring at room temperature the solution of the lithium derivative was added during 15 min to a suspension of 40 g (0.4 mol) of finely powdered anhydrous cuprous chloride in 50 ml of dry ether kept at -60°C . The green-coloured suspension was stirred at this temperature for 1 h and then allowed to attain room temperature overnight. The reaction mixture was finally heated with reflux for 1 h, cooled and the solid separated by centrifugation. Water was added, the product extracted with ether and dried (MgSO_4). Evaporation of the ether and distillation of the residue gave 8.5 g (87 %) of crude (92 %) **1b**. Fractionation through a spinning-band column gave pure **1b** (99 %); b.p. 76°C (3.5 mmHg), m.p. 43°C ; ν_{max} 1595 m, 880 cm^{-1} (C=C); $\delta(\text{CCl}_4)$ 1.09 (s, 18 H, *t*-Bu), 1.72 (s, 6 H, Me), 6.00 (s, 2 H, olef. H). (Found: C 86.44; H 13.45. Calc. for $\text{C}_{14}\text{H}_{26}$: C 86.51; H 13.49.)

E,E-2,5-Diphenyl-2,4-hexadiene (1c). A solution of 5.0 g (2.5 mmol) of *E*-1-bromo-2-phenyl-1-propene¹³ in 10 ml of dry THF was added to 0.61 g (2.5 mmol) of magnesium and catalytic amounts of mercuric chloride in 25 ml THF. The reaction temperature was kept below 40°C during the addition of the bromide (15 min). After 30 min at room temperature and 1 h reflux the reaction mixture appeared as a grey-coloured suspension. Hydrolysis of an aliquot gave 95 % α -methylstyrene. An additional 10 ml THF was added and the reaction mixture was

cooled to -60°C . 40 g (0.4 mol) of finely powdered anhydrous cuprous chloride was added portionwise with stirring. The reaction mixture was further stirred for 2 h at -60°C and allowed to attain room temperature overnight. The reaction was worked up as described under **1b**. Evaporation of the solvents gave 1.4 g (48 %) of pure (99 %) **1c**, m.p. $134-137^{\circ}\text{C}$ (lit.¹⁴ m.p. 138°C) λ_{max} 1590, 860 cm^{-1} (C=C); $\delta(\text{CCl}_4)$ 2.25 (s, 6 H, Me), 6.75 (s, 2 H, olef. H), 7.8 (m, 10 H, ar. H).

3,6-Dimethyl-3,5-octadiene (1d). To a suspension of 213 g (0.5 mol) of 3-methyl-2-pentenyl-triphenylphosphonium bromide prepared from 1-bromo-3-methyl-2-pentene and triphenylphosphine in 1000 ml of dry ether was added with stirring during 90 min 245 ml of 2.17 M ethereal methylolithium (0.52 mol). The deep red-coloured reaction mixture was stirred at room temperature for another 1 h and then cooled (ice). A solution of 37.4 (0.52 mol) of 2-butanone was added dropwise with stirring during 2 h. The reaction mixture was left stirring at room temperature overnight and then heated under reflux for 2 h. Triphenylphosphine oxide was filtered, and the ether solution was washed with water and dried (MgSO_4). Evaporation of ether and fractionation of the residue gave 58.6 g (85 %) of **1d**.¹⁶ b.p. 62°C (14 mmHg); GLC (20 % SE-30) showed the presence of 10 % *Z,Z*-, 40 % *Z,E*-, and 50 % *E,E*-isomers.

Preparation of bis-adducts. General. Solid potassium *t*-butoxide was prepared from potassium and *t*-butyl alcohol as described in the literature.¹⁷ The diene and dry pentane were added, and to the stirred slurry the calculated amount of bromoform was added dropwise at about -15°C . The mixture was stirred overnight at room temperature, hydrolyzed with dil. HCl and worked up in the usual way.

E,E-2,2,2',2'-Tetrabromo-3,3'-di-*t*-butyl-3,3'-dimethylbicyclopropyl (2b). Reaction of potassium *t*-butoxide [from 3.9 g (0.1 g at.) of potassium], 25 g (0.1 mol) of bromoform and 5.5 g (28 mmol) of the diene **1b** in 40 ml pentane gave 4.0 g (27 %) of the *meso* bis-adduct **2b**, m.p. 143°C from methanol; $\delta(\text{CCl}_4)$ 1.29 (s, 18 H, *t*-Bu), 1.53 (s, 6 H, Me), 1.70 (s, 2 H cyclopropyl H). (Found: C 35.89; H 4.99. Calc. for $\text{C}_{18}\text{H}_{28}\text{Br}_4$: C 35.71; H 4.87).

From another experiment on twice the scale 6.6 g (25 %) of **2b** was obtained, and distillation of the mother liquor gave 6.6 g of a liquid, b.p. $80-86^{\circ}\text{C}$ (0.5 mmHg) which consisted essentially of two isomers $\text{C}_{18}\text{H}_{28}\text{Br}_4$ in a ratio of 4:1 as shown by mass spectrometry and GLC. The isomers could not be separated by prep. GLC without decomposition.

E,E-2,2,2',2'-Tetrabromo-3,3'-dimethyl-3,3'-diphenylbicyclopropyl (2c). Reaction of potassium *t*-butoxide [from 8.0 g (0.2 g at.) potassium], 51 g (0.2 mol) of bromoform and 12 g (0.05 mol) of the diene **1c** in 200 ml pentane gave 12.8 g (44 %) of the *meso* bis-adduct **2c**, m.p. 180°C (decomp.) from petroleum ether-benzene; $\delta(\text{CCl}_4)$

1.83 (s, 6H, Me), 2.08 (s, 2 H, cyclopropyl H), 2.4 (m, 10 H). (Found: C 41.52; H 3.43. Calc. for $C_{20}H_{18}Br_4$: C 41.55; H 3.31).

2,2,2',2'-Tetrabromo-3,3'-diethyl-3,3'-dimethyl-bicyclopropyl (2d). Reaction of potassium *t*-butoxide (from 35 g (0.9 g at.) of potassium), 200 g (0.9 mol) bromoform and 41 g (0.3 mol) of the diene *1d* in 250 ml pentane gave 112 g (75 %) of the bis-adduct *2d*, m.p. 83–85 °C from methanol. (Found: C 29.93; H 3.91. Calc. for $C_{18}H_{18}Br_4$: C 29.91; H 3.76.) Thin layer chromatography on silicagel (pentane) revealed the presence of at least three isomers.

Reactions of bis-adducts with methylolithium.

General. The procedure was essentially as described previously.³ An ethereal solution or suspension of the bis-adduct was cooled to –70 °C and an ethereal solution of methylolithium was added drop-wise with stirring. After an hour, whereby the temperature rose to about –20 °C, water was added and the product isolated in the usual way.

2,2,3,8,9,9-Hexamethyl-3,4,6,7-decatetraene (3b). From reaction of 5.4 g (10 mmol) of adduct *2b* and methylolithium (40 mmol) in ether was obtained 2.0 g (91 %) of the *meso* diallene *3b*, m.p. 72 °C from methanol; ν_{\max} 1945, 810 cm^{-1} (C=C=CH–); λ_{\max} (heptane) 214 nm (42 000); $\delta(CCl_4)$ 1.08 (s, 18 H, *t*-Bu), 1.76 (m, 6 H, Me), 5.53 (m, 2 H, olef. H). (Found: M.w. 218; C 88.05; H 11.98. Calc. for $C_{18}H_{26}$ (218): C 88.00; H 12.00.)

2,7-Diphenyl-2,3,5,6-octatetraene (3c). From reaction of 7.0 g (12 mmol) of the adduct *2c* and methylolithium (40 mmol) in ether was obtained 2.8 g (90 %) of the *meso* diallene *3c*, m.p. 139 °C (decomp.) from petroleum ether; ν_{\max} 1930, 810 cm^{-1} (C=C=CH–); λ_{\max} (CHCl₃) 261 nm (53 500); $\delta(CCl_4)$ 2.18 (m, 6 H, Me), 5.97 (m, 2 H, olef. H), 7.2 (m, 10 H, ar. H). (Found: M.w. 258; C 92.69; H 7.29. Calc. for $C_{20}H_{18}$ (258): C 92.98; H 7.02.) The structure has been confirmed by X-ray crystallography.¹⁵

3,8-Dimethyl-3,4,6,7-decatetraene (3d). From reaction of 14.5 g (30 mmol) of the adduct *2d* and methylolithium (80 mmol) in ether was obtained 4.0 g (82 %) of the diallene *3d*, b.p. 45–47 °C (0.5 mmHg); ν_{\max} 1955, 820 cm^{-1} (C=C=CH–); λ_{\max} (heptane) 212 nm (42 600); $\delta(CCl_4)$ 1.01 (t, 6 H) and 1.95 (q, 4 H)(Et), 1.70 (m, 6 H, Me), 5.42 (m, 2 H, olef. H). (Found: M.w. 162; C 88.78; H 11.17. Calc. for $C_{12}H_{18}$ (162): C 88.82; H 11.18.)

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