Radical-induced Cyclizations of *cis*-1,10-Dichlorodec-5-ene and 1,10-Dichlorodec-5-yne

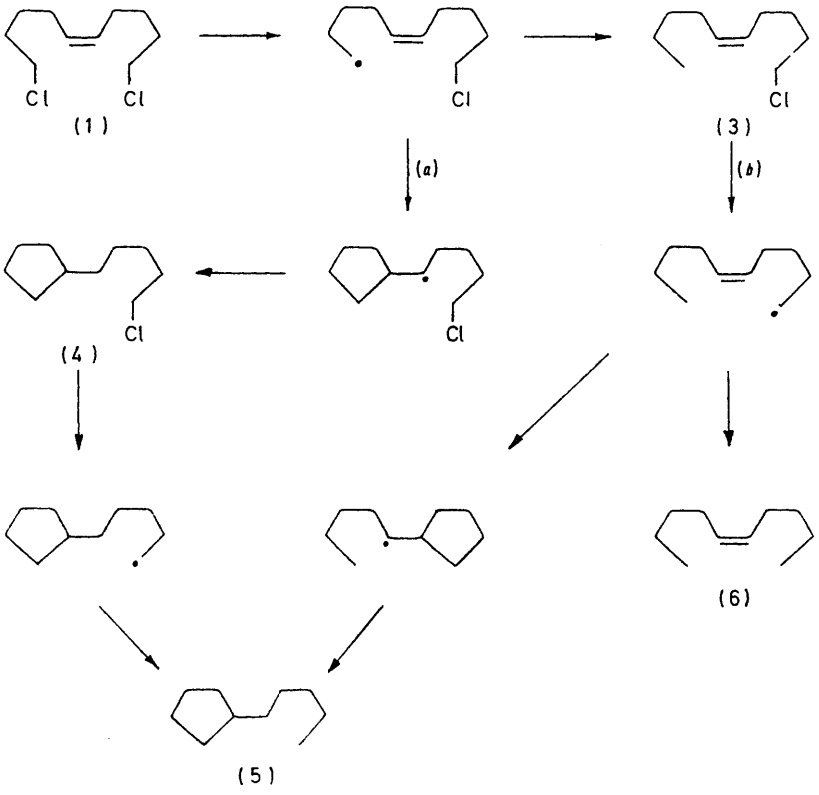
By **Stuart A. Dodson** and **Robert D. Stipanovic,*** Departments of Chemistry and Plant Sciences, Texas A & M University, and National Cotton Pathology Research Laboratory, P. O. Drawer JF, College Station, Texas, in co-operation with the Texas A & M Experiment Station

The radical reduction of *cis*-1,10-dichlorodec-5-ene and 1,10-dichlorodec-5-yne initiated by tributylstannane was studied. The products consisted of a series of mono-, bi-, and a-cyclic compounds. Formation of the monocyclic compound from the alkene proved to be a very ready reaction, consistent with a solvent cage effect.

An alkenyl or alkynyl radical possessing a double or triple bond in position 5 or 6 undergoes intramolecular cyclization affording a five- or six-membered hydrocarbon ring, or both.[1-6] The ease and direction of cyclization depend on the radical structure. With highly resonance-stabilized radicals, cyclohexyl derivatives are the major products, whereas primary alkyl radicals yield cyclopentylmethyl derivatives. We here report the reactions of *cis*-1,10-dichlorodec-5-ene (1) and 1,10-dichlorodec-5-yne (2) with various concentrations of tributylstannane.[7,8]

Free-radical intermolecular reactions were minimized by use of dilute solutions of reagents. In separate reactions, 1, 2, and 4 equiv. of tributylstannane were used. Azobisisobutyronitrile (AIBN) was used as the radical initiator (1·8 mole % based on the dihalide).

The alkene (1) and the alkyne (2) provided four and five



SCHEME 1

products, respectively, as determined by g.l.c. analysis. These products from the alkene (Scheme 1) and the alkyne (Scheme 2) and their relative amounts are listed in order of elution (g.l.c.) in Tables 1 and 2. They were subjected to g.l.c.–mass spectrometric analysis; their n.m.r. spectra were determined after isolation by preparative g.l.c.

The alkene appears to be significantly more reactive

[1] J. K. Crandall and D. J. Keyton, *Tetrahedron Letters*, 1969, 1653.
[2] M. Julia, *Accounts Chem. Res.*, 1971, **4**, 386.
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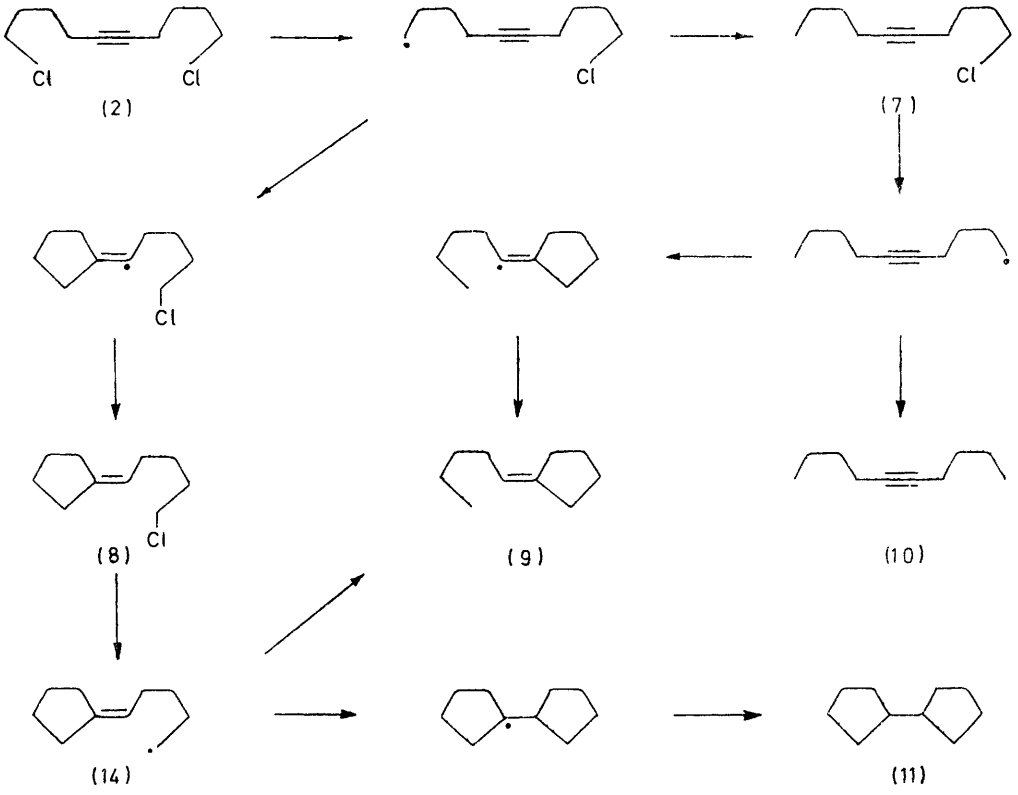
[4] A. L. J. Beckwith, *Chem. Soc. Special Publ.*, 1970, No. 24, p. 239.
[5] C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, 1972, **94**, 6059.
[6] A. L. J. Beckwith and G. Phillipou, *J.C.S. Chem. Comm.*, 1973, 280.
[7] H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Amer. Chem. Soc.*, 1962, **84**, 3584.
[8] H. G. Kuivila and L. W. Menapace, *J. Amer. Chem. Soc.*, 1964, **86**, 3047.

than the alkyne towards free-radical reaction in that it provided overall more cyclized material than the alkyne. This remained true for all the proportions of stannane used. At low stannane concentrations, the formation of cyclized products was favoured over simple reduction.

pentane to *cis*-dec-5-ene is unusually large. Preferential formation of cyclic hydrocarbon (5) may be caused by a solvent cage effect. Reaction of the 5-chloro-1-cyclopentylpentyl radical with tributylstannane may leave the tributylstannyl radical reasonably close to the



SCHEME 2

When only 1 equiv. of stannane was used in the reduction of the dichloroalkene (1), the cyclic hydrocarbon, n-pentylcyclopentane (5), comprised a significant part of

TABLE 1

Distribution of products from reduction of *cis*-1,10-dichlorodec-5-ene with tri-n-butylstannane (% of total reduced material)

Equiv. Bu_3SnH	Products (6) [a]	(5) [b]	(3) [c]	(4) [d]
1	1	25	12	62
2	7	63	8	22
4	15	44	21	20

[a] *cis*-Dec-5-ene. [b] n-Pentylcyclopentane. [c] *cis*-1-Chlorodec-5-ene. [d] 1-Chloro-5-cyclopentylpentane.

the total product (25%), whereas the amount of *cis*-dec-5-ene (6) was insignificant (1%). n-Pentylcyclopentane can be formed by either of two reaction pathways (Scheme 1): (*a*) free-radical reduction of 1-chloro-5-cyclopentylpentane (4) and (*b*) cyclization and reduction of 1-chlorodec-5-ene (3). Pathway (*b*) also leads to the straight-chain hydrocarbon dec-5-ene (6). Although it cannot be calculated exactly, the ratio of n-pentylcyclo-

[9] C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 2262.

chlorine atom, providing adequate opportunity for abstraction of the latter before the solvent cage breaks up.

Owing to the lower reactivity of the alkyne with respect to free-radical addition, the solvent cage effect is not as evident in the alkyne reduction (Table 2) with 1 equiv. of tributylstannane. An overall reaction mechanism for reduction of the alkyne is shown in Scheme 2.

Beckwith and Phillipou [6] recently reported that the radical (12) does not undergo intramolecular addition.

TABLE 2

Distribution of products from reduction of 1,10-dichlorodec-5-yne with tri-n-butylstannane (% of total reduced material)

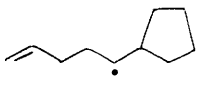
Equiv. Bu_3SnH	Products (10) [a]	(9) [b]	(11) [c]	(7) [d]	(8) [e]
1	2	5	11	29	53
2	16·5	16·5	18	28	21
4	42	20	14	18	6

[a] Dec-5-yne. [b] n-Pentylidenecyclopentane. [c] Bicyclopentyl. [d] 1-Chlorodec-5-yne. [e] 5-Chloropentylidenecyclopentane.

Walling and his co-workers found similar results with the pent-4-enyl radical (13).[9,10] Both these radicals undergo

[10] C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, 1966, **88**, 5361.

simple reductions with tributylstannane. Our work shows conclusively that the product radical (14) (Scheme 2) does behave as its acyclic analogue (hex-5-enyl radical) [10] and undergoes intermolecular addition to give bicyclopentyl (11). In the species (12) and (13), the radical position is separated from the terminal end of the double bond by two sp^3 and one sp^2 carbon atoms.



(12)

(13)

Molecular models indicate that free radicals such as (14) can approach to within bond-forming distance of the π-bond with very little σ-bond distortion. However, models of (12) and (13) show that approach of the radical centre to within bonding distance of the terminal double bond carbon atom results in considerable distortion of the σ-bond framework of the developing ring. This distortion is apparently sufficient to prevent ring closure from competing favourably with simple reduction, so cyclic products are not observed.

EXPERIMENTAL

I.r. spectra of liquids were obtained for films with a Beckman model 18A instrument. N.m.r. spectra were recorded with a Varian T60 or JEOL-MH-100 instrument for solutions in CCl_4 or $CDCl_3$ with Me_4Si as internal standard. Mass spectra were recorded with a Finnigan 1015 quadrapole spectrometer. Preparative and analytical g.l.c. were carried out with a Varian Aerograph 2800 instrument by use of a thermal conductivity detector and a 10 ft × ⅜ in 20% OV-1 column. Spectroscopic data are available as Supplementary Publication No. SUP 21219 (4 pp.) *

1,10-*Dichlorodec-5-yne* (2).—Gaseous ammonia (600 ml) was passed through a tower packed with potassium hydroxide pellets, and condensed at −78° in a flask equipped with a solid CO_2–acetone condenser, a drying tube, a stirrer, and a dropping funnel with a nitrogen inlet. Several crystals of iron(III) nitrate were added, followed by small pieces of sodium (9·4 g, 0·41 mol). 1-Chlorohex-5-yne (42·7 g, 0·37 mol) was added dropwise during 40 min. The mixture was stirred for 1 h at ammonia reflux temperature, after which 1-bromo-4-chlorobutane (63·4 g, 0·37 mol) was added dropwise during 1 h and the mixture was stirred at reflux for another 4 h. Anhydrous ether (250 ml) was added, and the ammonia was allowed to evaporate off overnight. Water (200 ml) was added cautiously, and the two layers were separated. After extraction of the water layer with ether, the combined extracts were washed with 10% hydrochloric acid and then with saturated aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). The solution was concentrated, and the residue was distilled on a spinning-band column to give 1,10-dichlorodec-5-yne (14·7 g, 19%), b.p. 124—126° at 5 mmHg (lit.,[11] 122—125° at 5 mmHg); δ 3·5 (4H, t; *J* 7 Hz) and 1·4—2·6 (12H, m).

cis-1,10-*Dichlorodec-5-ene* (1).—1,10-Dichlorodec-5-yne (6·21 g, 30·0 mmol), 5% palladium–barium sulphate (120 mg), and pyridine (60 ml) were hydrogenated at atmospheric pressure. The mixture was then filtered and acidified with 10% hydrochloric acid. The water layer was extracted with ether, and the combined extracts were dried ($MgSO_4$). The ether was removed, and the residue was distilled (short-path) to produce *cis*-1,10-dichlorodec-5-ene (6·1 g, 97%), >98% pure by g.l.c.; $\nu_{max.}$ 3005, 1650, and 645 cm^{-1}; δ 5·2—5·5 (2H, m), 3·5 (4H, t, *J* 7 Hz), and 1·1—2·3 (12H, m).

Reactions of the Alkene (1) *and the Alkyne* (2) *with Tributylstannane.*—A typical procedure is described for the reaction of *cis*-1,10-dichlorodec-5-ene (1) with 1 equiv. of tributylstannane.

To a solution of tributylstannane (2·91 g, 10·0 mmol) and AIBN (24 mg) in dry benzene (50 ml) was added a solution of *cis*-1,10-dichlorodec-5-ene (1) (2·09 g, 10·0 mmol) in dry benzene (50 ml). The mixture was refluxed with stirring and kept under nitrogen for 36 h. Most of the benzene was then distilled off, and the residue was subjected to g.l.c. analysis.

Products from cis-1,10-*dichlorodec-5-ene* (1). Four products were found; these are listed in order of their elution from g.l.c. (at 200°) in Table 1. They were isolated by preparative g.l.c. (first two at 125°; last two at 180°) and identified by their mass and n.m.r. spectra.

Products from 1,10-*dichlorodec-5-yne* (2). Five products were found; these are listed in order of their elution from g.l.c. (at 200°) in Table 2. They were isolated by preparative g.l.c. (first three at 125°; last two at 180°) and identified by their n.m.r. and mass spectra.

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

[11] D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, 1956, **78**, 2518.