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THE STEREOCHEMISTRY OF ALLENE DIMERIZATION: DIMERS OF 1-ADAMANTYL-3-CHLOROALLENE

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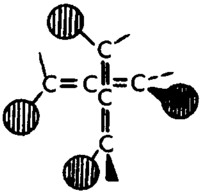
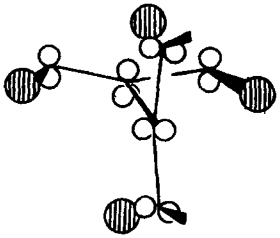
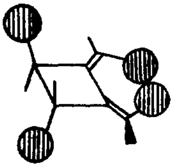
In the previous papers in this series[1,2] we have demonstrated that dimerization of acyclic allenes exhibits a stereoselectivity which favors the formation of those isomers in which the exocyclic methylene substituents take the inward, more crowded orientation. This stereoselectivity was attributed to favorable steric interactions in the orthogonal 2,2′-bisallyl biradicals leading to these crowded isomers.







Molecular models indicate that two adamantyl substituents cannot occupy the inward positions of these dimers so that an adamantyl-substituted allene should test to the fullest this inward-orienting stereoselectivity.

Treatment of 1-adamantyl-2-propyn-1-ol with thionyl chloride in dibutyl ether afforded a mixture of 1-adamantyl-3-chloroallene and 1-adamantyl-1-chloro-2-propyne, which was separated by column chromatography on silica gel in 38% and 24% yields, respectively. Dimerization of the allene was about 90% complete after twenty hours at 125-130° in solution in an equal weight of hexane; very little higher molecular weight material was present. The dimers were best separated by column chromatography on acidic alumina, and are shown in Figure I. Structures are based on the n.m.r. spectra of the dimers, given in Table I.

Figure I

Dimers of 1-Adamantyl-3-chloroallene

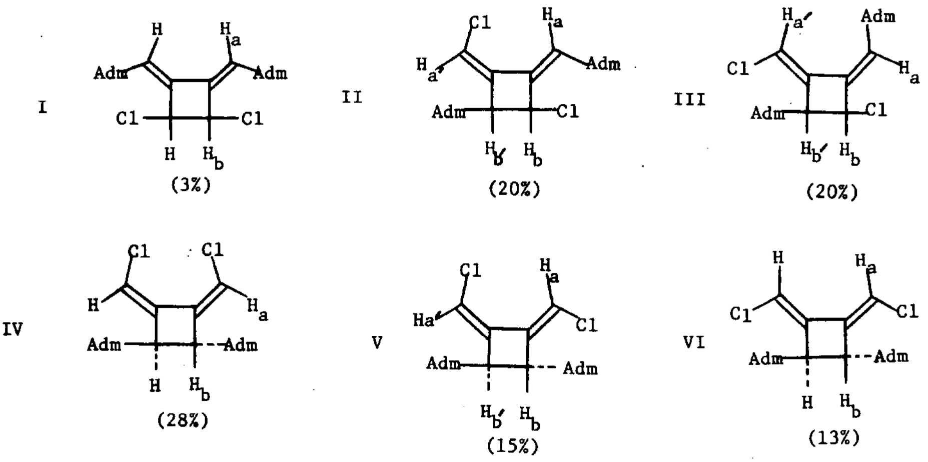


Table I Chemical Shifts of Dimers (τ)*

Dimer	a	a′	b	b′
I	4.47		5.13	
II	3.88	4.23	5.27	7.38
III	4.74	3.83	5.27	7.26
IV	4.35		7.80	
V	3.26	4.26	7.58	7.72
VI	3.90		7.25	

*Determined in CCl_4 with T.M.S. as internal reference

Dimer I is symmetrical, and its spectrum does not have a resonance in the range 7-8 τ, as would be expected if both adamantyl substituents were in the vicinal cyclobutyl positions, but does have the resonance typical of vicinal dichlorocyclobutyl dimers, at 5.13 τ. The adamantyl groups are therefore in the exocyclic positions. They have been drawn in outward orientation because a Dreiding model shows excessive crowding for inward orientation. The resonance of the vinyl hydrogens at 4.47 τ is not in disagreement with this orientation, but it does not establish it in the absence of the isomer having inward adamantyl groups. I appears to be the least crowded of all of these dimers, yet it is produced in very low yield.

This result would be expected if the stereoselectivity of the dimerization resulted from orientation of the biradical as shown, because twisting to break the allylic resonance of both allyl halves of the biradical would be required to yield I.

Dimers IV, V, and VI, on the other hand, do have resonances between 7.5-7.8 τ. Based *on the reported n.m.r. spectra of the dimers of 2,3-pentadiene*[3] *and 1,2-cyclononadiene*[4], the adamantyl cyclobutane substituents appear to be *trans*, since were they *cis*, the resonance should occur around 7.1 τ. This conclusion is in accord with expectations based on molecular models, which show that *cis* adamantanes would interfere with each other quite badly. The chlorines, then, must be in the exocyclic position, and all three possible combinations of orientations are found. Of the two symmetrical dimers IV and V, the former has its chlorovinyl resonance at 4.35, while in the latter it is at 3.90 τ. Inward vinyl protons have been found[1,3] to be deshielded relative to outward, and if this relation holds, the stereochemistries of IV and VI are as given. The unsymmetrical dimer, V, which must have one vinyl proton inward and the other outward, has resonances at 4.26 and 3.26 τ. The former corresponds to that found for outward protons in IV, while the latter, much further downfield than any of the others, is evidently the result of deshielding of the inward proton through steric compression[5] by the opposing inward chlorine.

Dimers II, and III, are unsymmetrically substituted, each with one vinyl chlorine and one vinyl adamantane. The assignment of resonances to each vinyl proton was aided by examination of their coupling with the corresponding cyclobutyl protons. In II the chlorovinyl resonance at 4.23 τ suggests an outward proton, and an adamantyl resonance at 3.88 τ (downfield ≃ 0.6 ppm from the inward protons of I as expected for compression by inward chlorine) suggests an inward proton. In III the chlorovinyl resonance is at 3.83 τ, so this proton is probably inward, with chlorine outward as in VI. The adamantyl resonance at 4.74 τ is 0.27 ppm upfield from the resonance of the inward protons of I, so this proton is probably outward, with the adamantyl group inward.

The relative stabilities of dimers IV, V, and VI were examined by iodine-catalysed isomerization of IV in toluene at 125-130°. The resulting dimer mixture, recovered in 33% yield after chromatography on basic alumina, was found to consist of IV, V, and VI in the ratio 1:13: 1.5, indicating that V is at least thirteen times as plentiful as IV under equilibrium conditions, although only half as much as is formed during dimerization.

Dimerization of 1-adamantyl-3-chloroallene is more complicated than of 1-chloro-3-mesitylallene.[1] The stereochemistry of the major dimers of the latter was rationalized as arising from the least crowded conformation of an orthogonal 2,2'-bisallyl biradical intermediate (larger substituents all inward, each end flat to preserve allylic resonance). The minor dimers can arise from a biradical only slightly more crowded: one mesityl outward, other substituents inward. Assuming (1) that only the less crowded conformations of such biradicals are produced (or involved in cyclization), (2) that the stereochemistry of ring substituents is controlled by the allowed conrotatory closure of the radicals, and (3) that excessive crowding prevents inward orientation of two adamantyl groups or of adamantyl and chlorine on the double bonds, five biradical conformations are required to account for dimers I-VI. These are the less crowded ones: all substituents inward, one outward and three inward, and two like substituents outward and two inward. The observation of preferential conrotatory opening of dimers of 1,2-butadiene[3] supports the second assumption, but it is also possible that *trans* isomers are formed because less twisting is required during closure to produce them or because they are more stable. Dreiding models suggest that two inward-oriented adamantyl groups on the biradical are not much less crowded than one inward and one outward. However, it is not easy to understand the absence of a dimer with *trans* ring chlorines and adamantyl groups unsymmetrically arranged, nor the low yield of I, on the basis that the relative yields of I-VI reflect to some extent the amounts of the five less-crowded biradical conformations. The relative stabilities of the possible biradical conformations from various disubstituted allenes will be discussed later.

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