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THERMAL DIMERIZATION OF RACEMIC AND OPTICALLY ACTIVE 2,3-PENTADIENE

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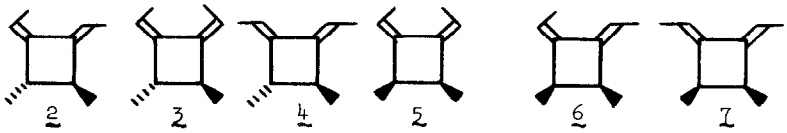
Dimerizations of mono- and 1,3-disubstituted allenes have received substantial attention in recent years,[1a,b] and some stereochemical aspects of the reaction are becoming clear. With halogen and phenyl substituted allenes, the 1,2-dimethylenecyclobutane products are formed with substituents on the ring being predominantly trans and with double bond substituents being syn, that is, directed inside the cavity of the cisoid diene system.[1b] This pattern was established with methyl as a substituent when all seven possible non-geminal dimethyl 1,2-dimethylenecyclobutanes from the dimerization of methylallene were identified and the distribution of these examined under conditions where product fractionation by subsequent reaction was minimal.[2] We wish to report further data on the stereochemistry of the allene dimerization using racemic and partially resolved[3] 2,3-pentadiene, 1, as a substrate.

Dimerizations of 1 were conducted in sealed tubes at 140° (allene to tube volume ratio 1:4). The dimer fraction from an intial 20-hr reaction was found to consist of six components on a di-n-butyltetrachlorophthalate (DBTCP) capillary vpc column. These components were separated on a preparative DBTCP column and were identified by their 220 MHz proton magnetic resonance spectra. The assignment of stereochemistry rests on comparison of chemical shift differences with those of the dimers of methylallene whose stereostructures were assigned chemically.[2] Thus, trans ring methyl groups are at lower field than cis ring methyl groups; trans ring hydrogens are at higher field than cis ring hydrogens; syn allylic methyls are at lower field than anti allylic methyls; vinyl protons on syn-ethylidene groups are at lower field than vinyl protons on anti-ethylidenes. The nmr spectra of the dimers are given in the table.

The distribution of dimeric products from simultaneous 19-hr reactions with racemic and optically active 1, $[\alpha]_D^{25} = +17.1°$ (neat), at 140° is listed in the table. Also listed are the results of an identical experiment run at 140° for only 1 hr. In a separate but comparable (allene to tube volume ratio, etc.) experiment optically active 1, $[\alpha]_{546}^{25} = +15.1°$

Table I. Distribution of Dimeric Products from Racemic and Optically Active 2,3-Pentadiene, 1, at 140°,[a] and Nmr[b] Spectra of the Products All Listed in Order of Emergence from DBTCP vpc Columns



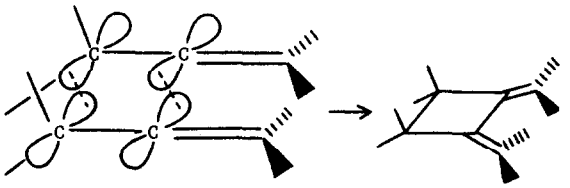
		2	3	4	5	6	7
		t,s,a	t,s,s	t,a,a	c,s,s	c,s,a	c,a,a
1 (rac)	19-hr rxn[c]	31.8 ± 0.8	47.7 ± 0.3[e]		10.8 ± 0.1	6.8 ± 0.2	1.6 ± 0.2
1 (act)	19-hr rxn[d]	32.6 ± 0.5	45.0		10.4 ± 0.3	7.4 ± 0.2	1.8 ± 0.3
1 (rac)	1-hr rxn[f]	29.3 ± 0.2	50.4 ± 0.8		11.2 ± 0.6	7.1 ± 0.4	1.2 ± 0.2
1 (act)	1-hr rxn[f]	32.9 ± 2.3	46.1 ± 3.2		13.6 ± 0.8	5.8 ± 0.2	1.8 ± 0.4
Ring Me H's[g]		1.08, 1.20	1.08	1.18	0.94	0.97, 1.05	1.07
Allylic Me H's[g]		1.65, 1.69	1.76	1.59	1.75	1.65, 1.69	1.59
Ring H's[h]		2.18, 2.36	2.19	2.19	2.74	2.88	2.99
Vinyl H's[i]		5.00, 5.46	4.91	5.34	5.02	5.00, 5.41	5.30

[a]The two 19-hr rxns were conducted simultaneously at nearly identical internal pressures. The same was true for the 1-hr reactions. [b]At 220 MHz in CCl_4 reported in ppm downfield from TMS. [c]1.3% of an unknown was also formed. [d]2.9% of an unknown was also formed. [e]As a 3:1 mixture of 3:4 by nmr. [f]Average of two runs. [g]Each signal was a doublet, J = 7 Hz. [h]Complex multiplets. [i]Each signal was a doublet of doublets, J = 7 and 2 Hz.

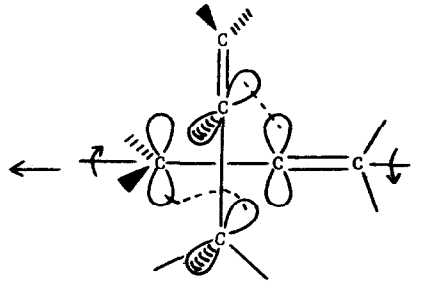
(c = 23 in $CHCl_3$), was heated at 140° for 1 hr, and 75% of 1 was recovered; it had $[\alpha]^5_{546}$ = + 14.7° (c = 23 in $CHCl_3$). Thus, 1 did not racemize substantially under conditions necessary to effect 25% dimerization of 1. Finally, in separate 1-hr and 20-hr dimerizations of optically active 1, $[\alpha]^{25}_D$ = + 17.1° (neat), 2 and the mixture of 3 and 4 were isolated, and the specific rotations of each were found to be + 0.5 ± 0.5° at 546 nm from both runs.

The data in the table reveal that formation of the trans-3,4-dimethyl-1,2-diethylidenecyclobutanes is favored by a factor of 4 over the cis materials, that within the trans family the ratio of syn,syn to syn,anti to anti,anti dimethyl substitution on the double bond is 3.0:2.5:1, and in the cis family the corresponding ratio is 7:4.5:1. These ratios should be contrasted with those from the dimethylenecyclobutanes derived from the methylallene dimerization where the ss to sa to aa ratio is 26:6:1;[2] it should also be noted that the trans to cis ratio of 3,4-dimethyl material from the methylallene dimerization is 6:1.[2]

The observation that the mixture of trans dimers, 3 and 4, formed from partly resolved 1 is essentially racemic is evidence against a "face to face", four-center interaction between two double bonds, a 2πs + 2πs cycloaddition,[4] in the allene dimerization since this process must give optically active 3 and 4 (albeit of opposite absolute configurations). A 2s + 2s cycloaddition[4] would require that 2 result from an interaction of opposite enantiomers of 1 and, therefore, it must be racemic; however, absence of activity in 2 is a necessary but not sufficient condition for intervention of this pathway; other pathways, particularly a 2s + 2a cycloaddition, can give the same result.



2πs + 2πs



2πs + 2πa

Recently, Moore[5] found that dimerization of about 90% optically pure 1,2-cyclononadiene gave substantially greater amounts of a meso dimer (equivalent to cis,anti,anti, 7) relative to a d-l material (equivalent to trans,anti,anti, 4) than in the dimerization of racemic 1,2-cyclononadiene. This result is consistent with an orbital symmetry allowed 2s + 2a cycloaddition, a reaction which in the cyclic case would allow formation of only the meso material from optically pure allene. If a 2s + 2a mechanism were operative in the dimerization of 1, possibly racemic 2, 5, and 7 should be obtained from one enantiomer of 1 while racemic 2, 5, and 7 as well as racemic 3, 4, and 6 should result from dimerization of racemic 1. The product distributions obtained from optically active 1 reflect to a small extent these predictions. But the 2,3-pentadiene used was only about 10% optically pure, and if one assumes a 2s + 2a pathway, a simple calculation reveals that the relative changes in product distributions from racemic and 10% optically pure 1 should be only one percentage point. Thus, the deviations expected were within the error limit of the analysis, and no proof of the intervention of the 2s + 2a pathway can be deduced from the product distribution. However, the 2s + 2a pathway predicts the formation of racemic 3 and 4 and possibly 2 from dimerization of optically active 1; these predictions are consistent with the results.

Also consistent with these results is a mechanism proceeding via 2,2'-bisallyl diradicals

which are formed non-stereospecifically, that is, by random rotations about the developing allylic radical termini; however, Moore's result[5] as well as other examples of stereospecific additions to allenes[6] cast doubt on this interpretation. On the other hand, the cycloaddition of acrylonitrile and optically active 2,3-pentadiene reported by Baldwin[7] which gives all four 2-methyl-3-ethylidenecyanocyclobutanes with the same configuration at C-2 cannot proceed via a 2s + 2a or a 2s + 2s cycloaddition if it is assumed that the acrylonitrile retains its stereochemistry. Thus, mechanistic alternatives to a 2s + 2a cycloaddition[8] might be necessary in the allene dimerization.

A number of additional questions remain unanswered in the allene dimerization. For instance, how is the 2,2'-bisallyl diradical related to the transition state for the dimerization? What is the relationship between the degenerate rearrangement of 1,2-dimethylenecyclobutane[2] and the dimerization? Why are syn-substituted exocyclic double bonds in the product favored in the dimerization? We hope to report on these matters in the future.

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