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RADICAL-ANION REACTIONS. THE REDUCTIVE DIMERIZATION OF 1,3-CYCLOHEXADIENE BY SODIUM-AMMONIA

D.Y. Myers, R.R. Grabbe and P.D. Gardner
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

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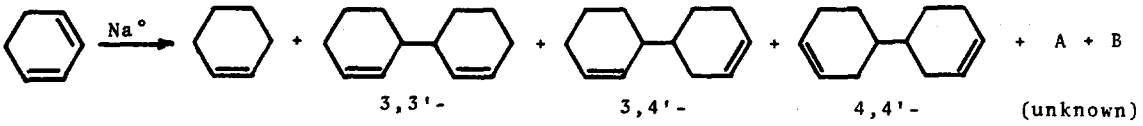
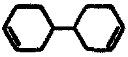
The reductive dimerization of a number of conjugated dienes by lithium-naphthalene in a variety of solvents has been reported but nothing bearing on reaction mechanism has been described.[1-3] We report here a study of the sodium-ammonia reduction of 1,3-cyclohexadiene[4] and some observations which explain why the reaction stops at the dimer stage rather than propagating to polymer.

The reduction of 1,3-cyclohexadiene with sodium in liquid ammonia-ether as conventionally run gave the expected[4] cyclohexene along with a small amount of a mixture of dihydro dimers. When done by inverse addition (adding Na-NH_3 from a Dewar-jacketed dropping funnel to a solution of the diene in refluxing ether-ammonia) dimer production improved substantially but with almost no polymer production. The results of four representative experiments are summarized in Table II and in the following abbreviated form. The mixture was separated



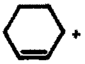
preparatively by glc using a 30 ft. x 1/4 in. SE-30 column. Structures of the three dihydro dimers were determined by mass spectral data summarized in Table I.

Table I

	m/e ratio 80/79	m/e ratio 81/79
	2.2	3.6
	1.2	1.8
	0.43	0.47


m/e 79


m/e 80


m/e 81

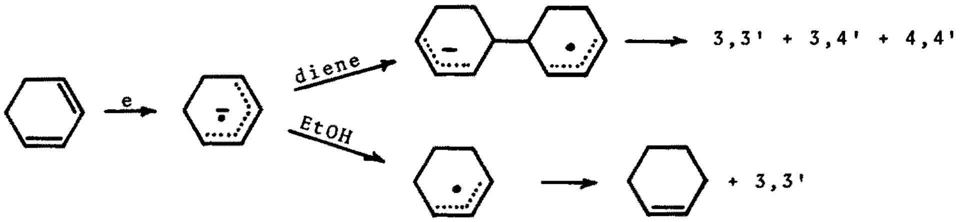
Ion 79 is a product of primary fragmentation, principally to the homoallylic cation, followed by loss of H_2 and 80 is from a McLafferty-type rearrangement. Ion 81 is the expected most abundant simple cleavage product from either 3,3' or 3,4' dihydro dimer. The relative abundance ratios constitute a clear-cut basis for structure assignment.

Table II

Run	diene/Na	EtOH/diene	Total Yield	Cyclohexene	Dihydro dimer 3,3'	Dihydro dimer 3,4'	Dihydro dimer 4,4'	Unknown A,B
1	1.3	—	90	31	32	25	2	1,1
2	1.2	18	100	60	40	0	0	0,0
3	10	—	99	11	33	31	9	5,10
4	10	18	93	46	34	12	0	1,0

The results of Run 1 may be regarded as "base-line" inverse addition data and reflect a mix of 1,3-cyclohexadiene radical ion chemistry with that of 3-cyclohexenyl radical resulting from protonation of the radical ion by NH_3. Run 2 shows the results of essentially completely protonating the radical ion and thus reveals the chemistry of just 3-cyclohexenyl radical. Experiments 3 and 4, in which a large excess of diene was used, provide data on the reaction of the radical ion and radical, respectively, with substrate.

It is quite clear that the radical ion is much more reactive than the radical toward additions to substrate. Even in the presence of a tenfold excess of diene, a minimum of 80% of the radical generated undergoes further reduction to cyclohexene or simply couples to give the 3,3'-dihydro dimer. By contrast, Run 3 shows that the radical ion adds readily to substrate to give a new radical ion in which the charge and the unpaired electron are separated. If this intermediate were to undergo addition of a second electron and double protonation in a purely statistical manner, the expected 3,3'/3,4'/4,4' distribution would be 1/2/1. The observed distribution of 3.7/3.4/1 suggests that these processes are not completely statistical and that the reaction was "contaminated" with radical roughly to the extent that Run 4 was "contaminated" with radical ion. Finally, the dimer radical ion more closely approximates a cyclohexenyl radical than it



does the monomer radical ion and would thus be expected to behave as such and not to add to another substrate to give trimer.

Although by-products A and B have not been identified, both are known to be dimeric.

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4. See A.J. Birch and G.S.R. Subba Rao, Aust. J. Chem., **23**, 1641 (1970) and references cited therein for a number of studies of reductions of other cyclohexadienes to monomeric reduced products.
5. Each dihydro dimer is presumed to be a mixture of the two diasteriomers even though it appeared to be a single substance by glc.