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THE "ANOMALOUS" COURSE OF SODIUM - LIQUID AMMONIA REDUCTION OF CYCLOALKYNES AND ITS INTERPRETATION

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THE reduction of dialkylacetylenes with sodium in liquid ammonia leads completely stereospecifically to the corresponding *trans*-alkenes.[1] The cycloalkynes behave differently, giving rise to mixtures of *cis*- and *trans*-cycloalkenes in various proportions.[2,3] The most striking case, as we have now found, is that of cyclodecyne which gives well over 90% of the *cis*-olefin.

Cope, Moore, and Moore[3] considered that the formation of the *cis*-cycloalkene could either result from "some change in the normal mechanism of *trans*-addition" (Path 1), or "be a consequence of a subsequent isomerisation of the *trans*-cycloalkenes" formed in the primary reduction process (Path 2). Path 2 has now been unambigously disposed of by our finding that *e.g.* *trans*-cyclodecene is completely stable under the

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[1] K.N. Campbell and B.K. Campbell, *Chem.Revs.* **31**, 77 (1942).

[2] M. Svoboda and J. Sicher, *Chemistry and Industry* 1959, 290.

[3] A.C. Cope, P.T. Moore, and W.R. Moore, *J.Amer.Chem.Soc.* **82**, 1744 (1960).

reduction conditions. There is, however, yet another possibility, namely that the acetylene rapidly rearranges to a diene, *e.g.* cyclodeca-1,2-diene, and that it is by the reduction of this diene that the *cis*-olefin arises (Path 3).

Moore and Ward[4] have now reported that cyclodecyne on treatment with sodium amide in liquid ammonia in part passes into cyclodeca-1,2-diene. Also, Devaprabhakara and Gardner[5] have found that cyclodeca-1,2-diene is reduced stereospecifically to *cis*-cyclodecene by sodium in liquid ammonia. In the light of these two findings Path 3 appears as a distinct possibility.

We have now followed in detail the course of reduction of cyclodecyne with sodium in liquid ammonia (Table).

TABLE

Reduction of Cyclodecyne with Sodium in Liquid Ammonia

Reaction Time (minutes)	PRODUCT COMPOSITION (in %)[6]			
	Cyclodecene *cis*	Cyclodecene *trans*	Cyclodeca--1,2-diene	Cyclodecyne
15	1	1	trace[7]	98
30	2	2	1	95
45	69	3	trace	28
60	88	2	trace	10
120	94	2	trace	4

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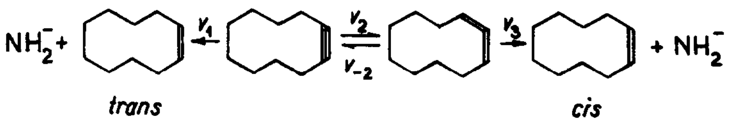
[4] W.R. Moore and H.R. Ward, *J.Amer.Chem.Soc.* **85**, 86 (1963).

[5] D. Devaprabhakara and P.D. Gardner, *ibid.*, **85**, 648 (1963).

[6] Determined by v.p.c. on silver nitrate-triethylene glycol by Mr. L. Baštář.

[7] Approximately 0.3 - 0.6 %.

Three significant facts emerge from the data listed : a) The *cis*/*trans* ratio varies strikingly with reaction time; b) there is a considerable "induction" period, the rate of disappearance of the acetylene at first being very slow (*cf*. product composition after 30 *vs* 45 minutes) c) cyclodeca--1,2-diene can actually be detected in the reaction mixture.[8] These facts, taken in conjunction with earlier findings,[4,5] are compatible with the following scheme :



$$\nu_2 > \nu_3 \gg \nu_1 \; ; \; \nu_2 \cong \nu_{-2} \quad \text{(cf.ref.4)}$$

According to this scheme the *trans*-isomer arises by (slow) direct reduction of the triple bond, the *cis*-isomer by way of the allene and its subsequent reduction. As the reduction proceeds sodium amide accumulates and the rate of acetylene - allene interconversion increases, accounting for observation *b* . The increased availability of the allene, the reduction of which affords the *cis*-olefin, in turn accounts for the increasing proportion of the *cis*-olefin as the reaction proceeds (observation *a*).

The data quoted up to now do not, however, eliminate the possibility that some proportion of the *cis*-olefin

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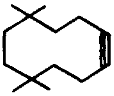
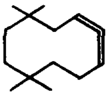
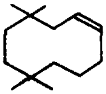
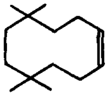
[8] The cyclodeca-1,2-diene was identified by v.p.c. on two different systems (silver nitrate, and tris-(cyanoethyl) glycerol) and by the presence of the characteristic peak at 1961 cm^{-1} in a fraction enriched in the diene.

arises directly from cyclodecyne by a *cis*-addition process, as envisaged by Path 1. From our work on derivatives of 1,1,4,4-tetramethylcyclodecane, which we shall report in detail later, we had available the cyclodecyne derivative I, m.p. 56-57°, as well as the cyclodecadiene II, which may be obtained from I by treatment with sodium amide in liquid ammonia.


I


II


III (cis)


IV (cis)

The acetylene I on reduction with sodium in liquid ammonia gives as the sole product the *cis*-olefin III, which is also exclusively formed, under the same conditions, from the diene II. The complete absence of the *cis*-olefin IV amongst the products of the reduction of I proves that a mechanism of *cis*-addition to the triple bond (Path 2) is not operative at all.