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GENERATION OF PERICYCLIC ANIONS BY LITHIUM REDUCTION OF BRIDGED DICYCLOPROPYL KETONES

Herman Bos and Gerhard W. Klumpp*

Scheikundig Laboratorium Vrije Universiteit, De Lairessestraat 174,
Amsterdam, The Netherlands

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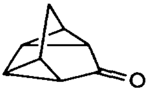
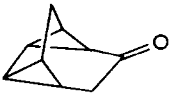
In the preceding paper we reported upon the two electron reductions by lithium in liquid ammonia, of the bridged dicyclopropyl ketones I-IV.

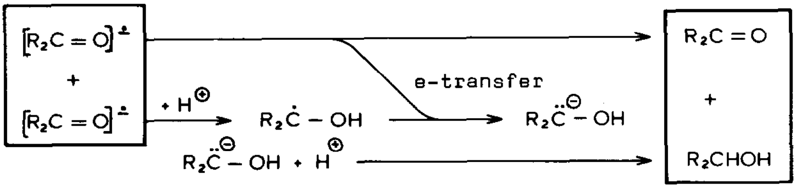

I


II


III


IV

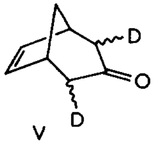
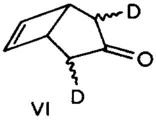
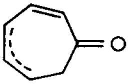
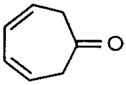
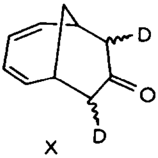
The double ring openings observed with ketones I-III were ascribed to the propensity for pericyclic interaction inherent in these compounds. In the present paper evidence is presented that the pericyclic interactions invoked are associated with the formation of carbanions. Our work is based on the recent finding by Rautenstrauch and Geoffroy[1] that treatment of non-enolizable and sterically hindered saturated ketones with metallic lithium in THF at -75°C leads to near-quantitative formation of solutions of the corresponding lithium ketyls, which are stable under these conditions. These authors also found that hydrolysis of these solutions yielded 1:1 mixtures of unchanged ketone and the corresponding alcohol. This finding (supplemented by the result of deuterium oxide quenching of the solutions) provides strong support for Scheme 1, which had been proposed earlier by House for the course of "dissolving metal reductions"[2].



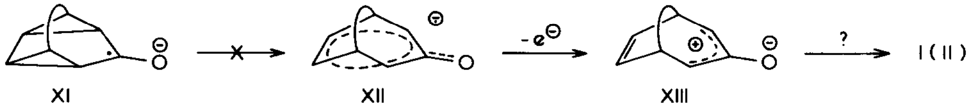
Scheme 1

According to Scheme 1 protonation of one molecule of ketyl triggers electron transfer from another molecule of ketyl, still unprotonated, thereby generating one molecule of starting ketone together with one α-hydroxycarbanion, which in a second protonation step yields the corresponding alcohol. Fundamentally the same behaviour as required by Scheme 1 was observed, when the bridged dicyclopropyl ketones I-III were subjected to the reaction conditions of Rautenstrauch and Geoffroy. Quenching of the yellowish solutions of the lithium ketyls of I-III (which were stable at -78°C practically indefinitely, as evidenced by the invariance of their esr-absorptions during long periods of storage) with deuterium oxide (or ethanol-O-d) produced starting ketone and reduction product in the molar ratio of ca. 1:1[3]. Products of reduction were the same doubly ring-opened ketones that were obtained (or invoked as precursors of the corresponding alcohols) in the lithium ammonia reductions of I-III. In addition the dihydroketone VI derived from II was accompanied by varying amounts of its monocyclic isomers VII-IX (see Table 1)[4]. The bicyclic ketones V, VI, and X contained between 1.5 and 2 atoms of deuterium per molecule.[5]

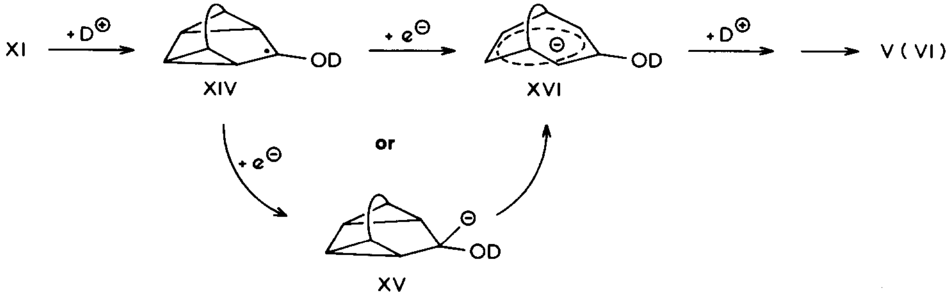
Table 1. Results of deuterolysis of THF solutions of the lithium ketyls of I-III at -78°C.
A: Ratio starting ketone (recovered) : reduction product(s)
B: Total yield [recovered starting material + reduction product(s)]

Substrate	Product(s)	A	B
I	 V	1:1.01 (±0.04)	60
II	 VI  VII/VIII  IX	1:0.98 (±0.15)	18
III	 X	1:0.88 (±0.05)	55

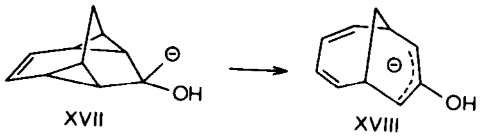
Details of the structures of the ketyls are not yet known. However, the regeneration of unchanged dicyclopropyl ketones upon protonation is most simply understood by assuming that the original structures of the ketones are largely preserved in the ketyls derived therefrom. If double ring opening had already taken place to a considerable degree on the ketyl stage (e.g. XI→XII) regeneration of I (II) from XII would involve the bishomoantiaromatic species XIII and the symmetry-forbidden process XIII→I (II).[6]



Adopting the validity of Scheme 1 it is therefore most probable that in the case of I and II the ring-opened product originates via the deuteroxybishomocyclopentadienyl anions XVI, whose formation is triggered by electron transfer to the deuterated ketyls XIV:



If the unrearranged anions XV are intermediates in this process at all, their rearrangement to XVI must be extremely fast, since it competes most successfully with protonation even at -78°C in THF or under the conditions of reduction by lithium in liquid ammonia (see preceding paper).[7]



In the case of III the rearrangement XVII→XVIII must either be a very fast stepwise process or proceed through a bishomoantiaromatic transition state. In conclusion we note: Double ring opening of "pericyclic" dicyclopropyl ketones, under conditions which allow formation and proton induced disproportionation of their ketyls, <u>can</u> be evidence of the transient existence of the corresponding pericyclic carbanions or the related transition states. However, absence of double ring opening under these conditions *is* evidence of the non-existence of such interactions.[8]

References and footnotes

1) V. Rautenstrauch and M. Geoffroy, J. Amer. Chem. Soc., 98, 5035 (1976).

2) Cf. H.O. House, "Modern Synthetic Reactions", 2nd ed., W.A. Benjamin, Menlo Park, Calif., 1972, chapter 3.

3) That these ratios are not the result of incomplete transformation of the starting ketones into their ketyls was demonstrated in two ways. (1) When reactions of ketones with excess lithium in THF were carried out in the presence of small amounts of preformed biphenyl radical anion the original blue-green colour disappeared immediately upon addition of the ketone. Its reappearance after a certain period of time was taken to signal the point where all ketone had been transformed into ketyl.
(2) After quenching a sample of a reaction mixture (containing excess lithium) had yielded the near 1:1 ratio of starting material and reduction product a fresh amount of ketone was added to the remainder of the original mixture. After allowing for another reaction period quenching again yielded the near 1:1 ratio, indicating that the newly added ketone had been affected in the same manner as the ketone present from the beginning.

4) Quenching with C_2H_5OD produced ratios of VI:(VII+VIII+IX) between 1 and 4. Using D_2O the values of these ratios decreased to between 0.1 and 0.6. The origins of this phenomenon are not yet clear.

5) Deviations from the ideal value 2 are ascribed to the extreme difficulty of avoiding traces of moisture when carrying out ketyl reactions at -78°C on the small scale (0.5 mmole) at which the present experiments were performed.

6) (a) Concerning the reluctance of various bicyclooctadiene derivatives to form bishomocyclopentadienyl cations, see: A.F. Diaz, M. Sakai, and S. Winstein, J. Amer. Chem. Soc., 92, 7477 (1970); H. Hart and M. Kuzuya, ibid., 98, 1545 (1976).
(b) No products of intramolecular cycloaddition (e.g. I) were observed, when 2,4-dibromobicyclo[3.2.1]oct-6-en-3-ones were subjected to conditions which normally lead to oxyallyl cations from α,α'-dibromo ketones (H.M.R. Hoffmann, private communication, see also: H.M.R. Hoffmann and M.N. Iqbal, Tetrahedron Letters, 1975, 4478).

7) For another case of very rapid formation of the bicyclo[3.2.1]octa-2,6-dien-4-yl anion, see: W.G. Dauben and R.J. Twieg, Tetrahedron Letters, 1974, 531.

8) Since all hydroxycarbanions invoked in the present work protonate at the carbon atoms α to the carbonyl group, γ-protonation (which must obtain if only a single cyclopropane ring of a dicyclopropyl ketone were opened) is considered inconsistent with a species formed by pericyclic delocalization.