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RING OPENING IN THE REACTION OF DIPHENYLCYCLOPROPANE DERIVATIVES WITH STRONG BASE: EVIDENCE FOR A PROTON TRANSFER AND AGAINST AN ELECTRON TRANSFER INITIATED REACTION. FACILE DISROTATORY RING OPENING OF A CYCLOPROPYL ANION AT -75°C

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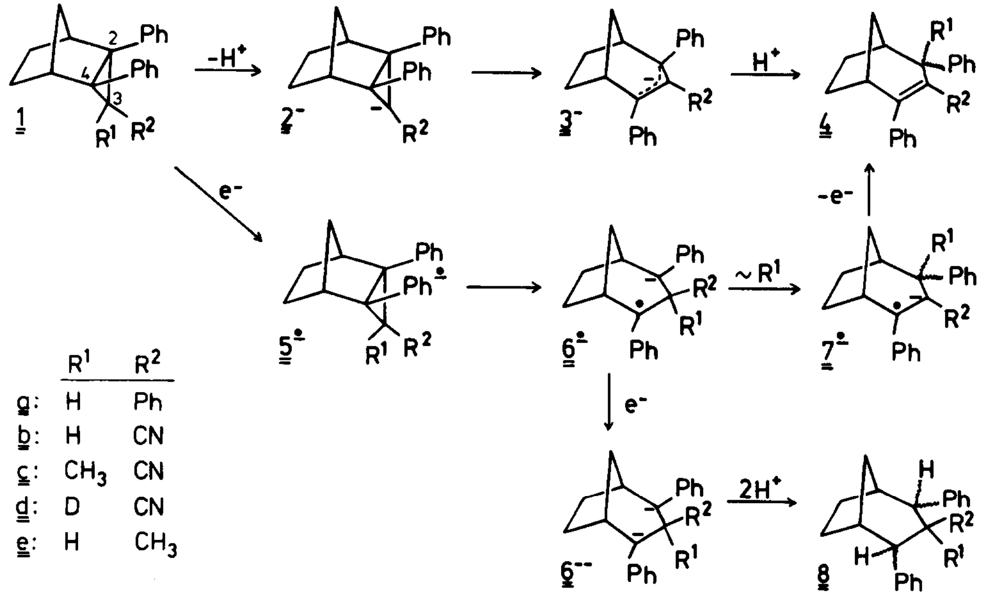
The reaction of cyclopropanes like 2,3,4-triphenyl-endo-tricyclo[3.2.1.$0^{2,4}$]octane (1a) with base is initiated by proton and not by electron transfer. The facile disrotatory cyclopropyl anion ring opening reaction of 2^-(R^2=CN, M^+=Li^+) at -75°C does not occur synchronously.

2,3,4-Triphenyl-endo-tricyclo[3.2.1.$0^{2,4}$]octane (1a) isomerizes in the presence of potassium tert-butoxide (KO-t-Bu) in dimethyl sulfoxide (DMSO) (70°C, 20 h) to 2,3,4-triphenylbicyclo[3.2.1]oct-2-ene (4a)[1]. The reaction was originally[1] interpreted to proceed via forbidden disrotatory ring opening of the cyclopropyl anion 2^-(R^2=Ph, M^+=K^+) to the allyl anion 3^- (R^2=Ph, M^+=K^+) (Scheme I). Other authors concluded later[2] that "the reaction of 1a with KO-t-Bu in DMSO or hexamethylphosphoricacid amide (HMPA) (25°C, 24 h), or with dimsylpotassium in DMSO (70°C, 24 h) appears to proceed by a radical pathway". It was proposed that an initial single electron transfer (SET) from base to 1a affords $5a^{\dot{-}}$(M^+=K^+) which opens to $6a^{\dot{-}}$(M^+=K^+). The latter was envisaged to rearrange to $7a^{\dot{-}}$(M^+=K^+) which loses an electron, "possibly to 1a", to give 4a[3].

Scheme I

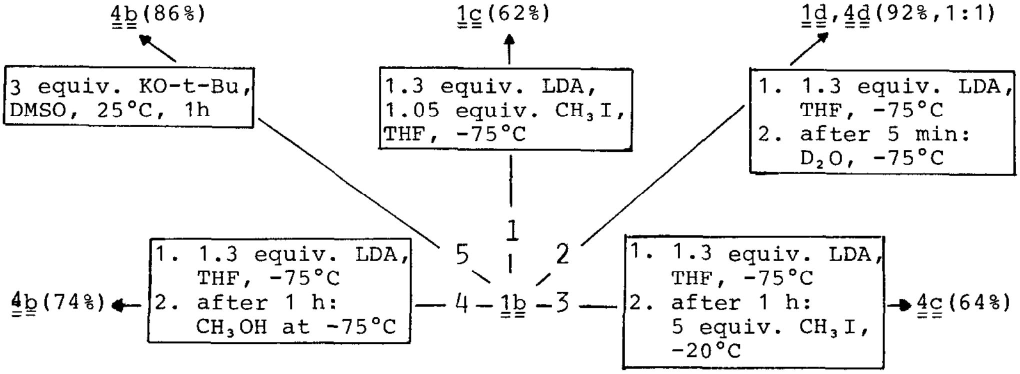


	R^1	R^2
a:	H	Ph
b:	H	CN
c:	CH_3	CN
d:	D	CN
e:	H	CH_3

In this work we demonstrate by means of 1a-c and 1e that transformations like 1a → 4a, initiated by base, require an acidic H^3; if H^3 is not acidic, or if C^3 is a quarternary carbon neither rearrangement to 4 nor reduction to 8 is observed (Scheme I). 8, however, is formed with alkali metals or sodium naphthalenide ($Na^+N^{\dot{-}}$).

Scheme II[5] summarizes the reactions of the tricyclic nitrile 1b.

Scheme II



It is evident from reactions 1-4 that the cyclopropyl anion 2^-(R^2=CN, M^+=Li^+) transforms completely and in a disrotatory (!) manner into the allyl anion 3^-(R^2=CN, M^+=Li^+) at -75°C within 1 h[6,7]! Reaction 5 is the same type of rearrangement with the same base system as in the case of 1a[1,2]; the relative rates and temperatures, however, are strikingly different: the formation of 4a takes 20 h at 70°C[1,2], that of 4b is complete in only 1 h at 25°C. In view of reactions 1-4 and the fact that cyclopropyl nitriles[8] are much stronger acids than phenyl=cyclopropanes[9], it is valid to assume that the formation of 4b with KO-t-Bu in DMSO also follows the cyclopropyl/allyl anion pathway[10].

Further support for this pathway is provided by the facile rearrangement of 1a to 4a with 1.3 equiv. "superbase" potassium 3-aminopropylamide (KAPA) in 1,3-diaminopropane[11]: after 5 min at 25°C a 67:33 ratio of 4a to 1a is observed, and at 0°C, 1a was completely transformed into 4a after 1 h[12].

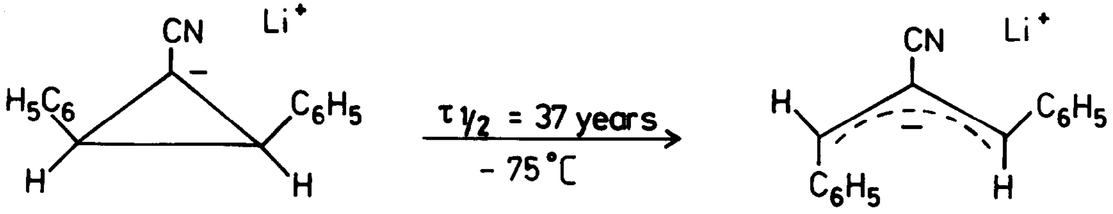
A totally different picture emerges for 1c[5] and 1e[5]. Treatment of 1c with base (LDA, THF, -75°C, 1 h; KO-t-Bu, DMSO, 25°C, 24 h; KO-t-Bu, DMSO, 70°C, 5 h) leads to complete recovery of starting material[10]. Similarly, 1e is also unreactive towards base (KO-t-Bu, DMSO, 70°C, 6 h; KAPA, 1,3-diaminopropane, 25°C, 24 h). Thus, replacing the acidic H^3 in 1b by a methyl group as in 1c, or by making H^3 relatively non-acidic as in 1e[8b], prevents proton transfer and therefore leads to no reaction with base. With a SET reagent (Na/K alloy, THF), however, 1e is transformed into 8e[5] in a manner analogous to the transformation of 1a to 8a by sodium naphthalenide[2].

In summary: The reactions of 1a-c and 1e with several base systems clearly show that proton transfer to the base is strongly preferred to electron transfer from the base[13].

What is the mechanism of the facile ring opening to give, e.g., the allylanion 3^-(R^2=CN,

$M^+=Li^+$) at -75°C within 1 h (reactions 2 and 4, Scheme II)?

The high energy, symmetry imposed barrier for disrotatory cyclopropyl → allyl anion isomerizations has been an important point against this step in the reaction 1a → 4a[2]. Even for the conrotatory mode of the cyclopropyl → allyl anion isomerization, which has never been observed for the parent compound, one calculates a high activation energy (kcal/mole): 31.2 (MINDO/3); 66.7 (STO-3 G); 38.0 (4-31 G)[6a]. These data are confirmed by the cis-2,3-diphenylcyanocyclopropyl anion (9^-Li^+) which is nicely suited for a comparison with 2^-(R^2=CN, $M^+=Li^+$): from the rate constant at -11.1°C ($k_1 = 2.21 \cdot 10^{-4} s^{-1}$; $E_A = 20.7$ kcal·mole^{-1})[6a] a halflife of 37 years (!) is extrapolated for the conrotatory (!) ring opening to the allyl anion 10^-Li^+ at -75°C!



9^-Li^+ 10^-Li^+

Hence it is unlikely that 3^-(R^2=CN, $M^+=Li^+$) is formed synchronously from the cyclopropyl anion 2^-(R^2=CN, $M^+=Li^+$) even though the transformation 2^- → 3^- is probably favored by ring strain[2,6a].

Therefore, and since it has been observed in recent years that in reactions of carbon acids with all kinds of base systems carbanions are formed which are very often better electron donors for SET reactions than the base[13] we currently investigate the following mechanistic alternatives: (1) a bimolecular SET process of the cyclopropyl anion 2^-(R^2=CN, $M^+=Li^+$) with the cyclopropane 1b to give the cyclopropyl radical $2^{\bullet}$(R^2=CN) and the cyclopropyl radical anion $5b^{\dot{-}}$($M^+=Li^+$). Both, cyclopropyl radicals[14] and cyclopropyl radical anions[15] are known to open the ring easily. Electron transfer from the trimethylene radical anion $6b^{\dot{-}}$($M^+=Li^+$) to the allyl radical $3^{\bullet}$(R^2=CN) and proton abstraction should lead to the allyl anion 3^-(R^2=CN, $M^+=Li^+$); (2) an intramolecular SET process of the cyclopropyl anion 2^-(R^2=CN, $M^+=Li^+$) which should be comparable to that of the elusive nitrocyclopropyl anion[16,17].

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