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1,3-DIPHENYLALLYL ANION: PREPARATION OF THE UNSTABLE (Z,E)-ISOMER

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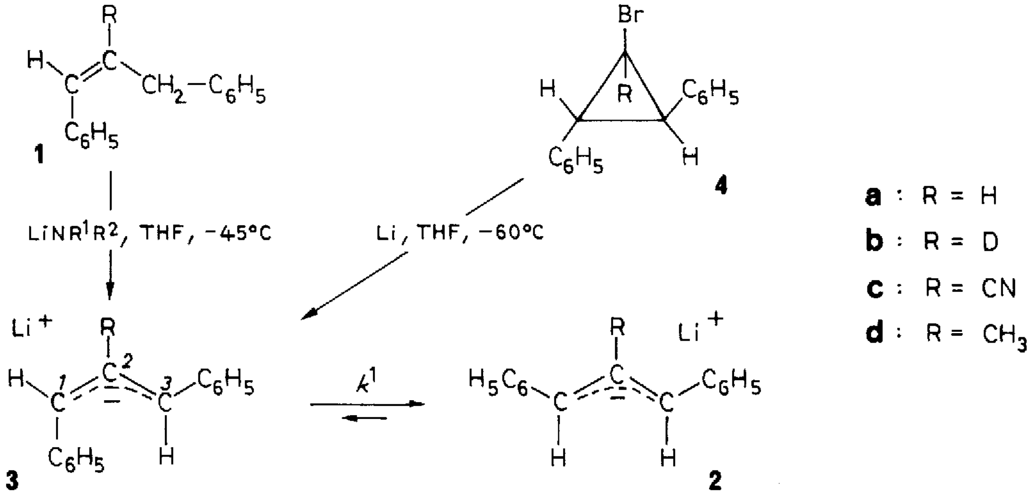
Deprotonation of *cis*-1,3-diphenylpropene (**1a**) led only to (E,E)-1,3-diphenylallyl anion (**2a**) instead of the expected (Z,E)-1,3-diphenylallyl anion (**3a**) when the reaction was performed with n-butyllithium in THF/hexane even at -30°C.[1]



We wish to report the preparation of the less stable (Z,E)-1,3-diphenylallyl anion (**3a**). This provides to the best of our knowledge the first example of an allyl anion system in which two isomers have been obtained separately.

(Z,E)-**3a** was accessible in two ways:

1. Reaction of lithium cyclohexyl-isopropylamide ($LiNR^1R^2$) as base[2] with **1a**[3] in THF at -45°C.[4]
2. Reaction of lithium metal with 1-bromo-*cis*,*trans*-2,3-diphenylcyclopropane[5,6] (**4a**) in THF at -60°C.[7]

The (Z,E)-configuration of **3a** is shown by means of the nmr spectrum of the anion with perdeuterated phenyl-substituents[8]: δ (ppm in THF) 4.40 (d, 1 H, J = 10.0 Hz, 1-H), 5.35 (d, 1 H, J = 14.5 Hz, 3-H), 6.60 (dd, 1 H, J = 10.0 and 14.5 Hz, 2-H). Accordingly, the protonation of **3a** with HCl/THF at - 60°C afforded a nearly 1:1 mixture of *cis*-propene **1a** and its *trans*-isomer.

The rate of isomerization was followed by nmr. From the rate constants k_1 (sec^{-1}) = $6.4 \cdot 10^{-5}$ (-55°C), $1.7 \cdot 10^{-4}$ (-49°C), $2.1 \cdot 10^{-4}$ (-48°C), $5.1 \cdot 10^{-4}$ (-43°C), $7.7 \cdot 10^{-4}$ (-40°C) and $1.4 \cdot 10^{-3}$ (-37°C) the activation parameters $\Delta H_1^{\ddagger} = 17.3 \pm 1.8$ kcal/mol and $\Delta S_1^{\ddagger} = 2.0 \pm 8$ e.u. were calculated. The rate constant k_1 at -40°C corresponds to $\Delta G_1^{\ddagger} = 17.0$ kcal/mol and to a half-life $\tau_{\frac{1}{2}} = 15$ min at this temperature. The half-life of 2.9 min at -30°C, extrapolated from the above data, explains the difficulty in observing the unstable (Z,E)-isomer **3a** before it rearranges to the (E,E)-isomer **2a**[1].

Furthermore, with the nmr spectrum of (Z,E)-**3a** in hand, we were able to detect this isomer in equilibrium with its more stable (E,E)-isomer **2a**. Determination of the equilibrium constant K was performed with the 2-deuterated allyl anions **2b** and **3b**. In (Z,E)-**3b** the two signals of H^1 and H^3 in the nmr appear as singlets which allows a more accurate determination of K. The equilibrium was established from both isomers. The unstable anion **3b** was prepared from **4b**; pure **2b** resulted from deprotonation of *trans*-1,3-diphenyl-2-deutero-propene with lithium cyclohexyl-isopropylamide in THF at -45°C. The following equilibrium constants have been measured: K (±2) = 17 (-30°C), 12 (-20°C), 10 (-10°C), 9 (0°C) and 8 (17°C)[9,10]. Thus, $\Delta\Delta G_{0\,(17^{\circ}C)}$ between (Z,E)-**3a** and (E,E)-**2a** only amounts to 1.2 kcal/mol.

The above results are significant in relation to the following points:

1. Remarkably, in the 1,3-diphenyl-2-*cyano*- and in the 1,3-diphenyl-2-*methyl*-allyl anion the phenyl groups prefer the *endo*,*exo*-position ((Z,E)-**3c** and (Z,E)-**3d**, respectively)[11,12]. Other isomers had not been reported so far. However, a close examination of the nmr spectra of (Z,E)-**3c** and (Z,E)-**3d** in THF at temperatures below -15°C and -30°C, respectively, reveals the existence of ~8%

of the less stable isomers in equilibrium with the more stable ones. At temperatures around -5°C the signals of the less stable isomers broaden due to participation in the topomerization of (Z,E)-3c and (Z,E)-3d[13].

2. The topomerization of the (Z,E)-1,3-diphenyl-2-cyanoallyl anion (3c $\rightleftharpoons$ 3c) requires a free energy of activation $\Delta G^{\ddagger}_{62^{\circ}C}$= 16.5 kcal/mol[11]. The similar value of $\Delta G^{\ddagger}_{1\ (62^{\circ}C)}$ = 15 ± 1 kcal/mol[14] for the single rotation of (Z,E)-3a to give (E,E)-2a again supports the conclusion[11] that the mechanism of this topomerization is due to two consecutive single rotations with (Z,Z)-2c as an intermediate.

3. Since 1,3-diphenylallyllithium in THF exists as a solvent separated ion pair in the ground state[15] and since the transition state of the isomerization of lithium-(Z,E)-3a to give lithium-(E,E)-2a in THF corresponds to a benzyllithium type species which also is known to exist in THF as solvent separated ion pair[16], the gegenion should not influence the rotational barrier of the allyl system in the 1,3-diphenylallyl anion. This is in agreement with the result found in the case of the 1,3-diphenyl-2-cyanoallyl anion (3c): the rotational barrier of 3c is the same with the gegenions Li^+, Na^+ and K^+, respectively, in DMSO and with Li^+ in THF.

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2. M.W.Rathke and A.Lindert, J.Amer.Chem.Soc. 93, 2318 (1971)
3. cis-1,3-diphenylpropene (1a) was prepared by reaction of phenylacetaldehyde, benzyltriphenylphosphoniumchloride and 50% aqueous-NaOH, following a procedure of G.Märkl and A.Merz, Synthesis 1973, 295, and isolated by

low-temperature crystallization from methanol.

4. While deprotonation of **1a** with lithium cyclohexyl-isopropylamide is completed within 5 min. at -45°C, the reaction with n-butyllithium is too slow at this temperature compared to the anion isomerization **3a** → **2a**.
5. 1,1-dibromo-*trans*-2,3-diphenylcyclopropane[6] was reduced with triphenyltinhydride to give 1-bromo-*cis*,*trans*-2,3-diphenylcyclopropane.
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7. A study of the mechanism of this reaction will be published elsewhere.
8. In the parent (Z,E)-1,3-diphenylallyl anion (**3a**) the nmr signal of 2-H is hidden by the signals of the ortho and meta phenyl protons. The decadeuterated 1,3-diphenylallyl anion was prepared from decadeutero-cyclopropylbromide **4a**[5,6], which was obtained from decadeutero-*trans*-stilbene.
9. The presence of (Z,E)-**3a** together with (E,E)-**2a** explains the early findings of Freedman[1], confirmed by us, that protonation of the allyl anion solution leads to a 97:3 mixture of *trans*:*cis*-1,3-diphenylpropene.
10. Dr.R.J.Bushby, University of Leeds, has informed us, that he has detected 8% (Z,E)-**3a** besides 92% (E,E)-**2a** in liquid ammonia, gegenion Na^+; δ(ppm) 4.28 (d, 1 H, J 10.2. Hz, 1-H), 5.23 (d, 1 H, J 13.8 Hz, 3-H).
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