controls showed that the onset of isomerization coincided with the beginning of adduct formation. Under the same conditions without any triyne present, starting material was recovered unchanged. It is tempting to associate the biradicaloids[17] **3** and/or **4** with the catalytically active species in the maleate–fumarate interconversion, although clearly other radical mechanisms are possible.[18] Clarification of this point will have to await further studies.

Current efforts are directed toward the isolation of **2**, the design of labeling experiments to identify the nature of the precursor to **7**, and the use of **1** as a template for organometallic transformations.

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(11) Although we cannot rigorously rule out the presence of a very small amount of **2** in equilibrium with **1**, the calculations, the absence of absorptions in the ^{13}C and ^{1}H NMR spectra attributable to **2**, the similarity of the electronic spectrum with the corresponding spectra of other cyclic oligoacetylenes,[10] and the stability of **1** to reaction conditions that would be expected to lead to destruction of the four-ring argues strongly for the presence of pure **1** in solution.
(12) For comparison, the ^{13}C NMR spectrum of 2,6-octadiyne shows absorptions at 19.73, 75.80, and 77.67 ppm.
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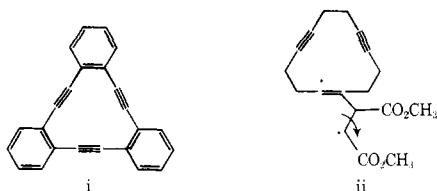
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Topomerization of the (Z,E)-1,3-Diphenyl-2-cyanoallyl Anion

Sir:

Three points are of interest in connection with the topomerization of allyl anions: the geometric stability of the allyl anion, its ionic character, and the mechanism of the topomerization. The investigation of the (Z,E)-1,3-diphenyl-2-cyanoallyl anion (**1**) together with semiempirical and ab initio calculations provides pertinent results.

Ring opening of 2-cyano-*cis*-2,3-diphenylcyclopropyl anion (**2**) (or of the trans isomer[1,2]) afforded **1** (Scheme I), which was identified by its NMR spectrum at 5 °C. Especially the high-field absorption of the phenyl protons in para position at δ 6.5 ppm is diagnostic of the ionic character[3–6] of **1** (sodium salt in Me$_2$SO). The (Z,E) configuration[7] is revealed by the different absorptions of H^1 and H^3 at δ 5.4 and 4.65 ppm, respectively.[8]

On warming, a broadening and, at 62 ± 3 °C, the coalescence of the signals of H^1 and H^3 are observed. This is indicative of a process that exchanges the environments of these hydrogens. From a lineshape analysis[9] the following kinetic data were calculated: $k_{62°C} = 100\,\text{s}^{-1}$; $\Delta G^{\ddagger}_{62°C} = 16.5$ kcal/mol; $\Delta H^{\ddagger} = 12.5 \pm 4.0$ kcal/mol; $\Delta S^{\ddagger} = -12 \pm 8$ eu. Concerning the mechanism of this exchange process, the following cases have to be considered.

(1) The reaction proceeds via cyclopropyl anion **2** as an intermediate (Scheme I). This is attractive since the thermal cis–trans isomerization of butadiene is dominated by a valence isomerization via cyclobutene.[10] Likewise, according to ab initio calculations[11] the 2-methylallyl cation should prefer to topomerize via the 1-methylcyclopropyl cation rather than by rotation around the allyl cation bond.
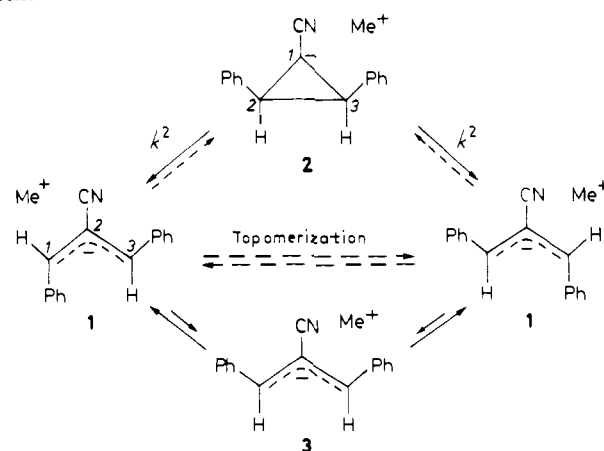
Scheme I

Table I. Calculation of the Activation Energy (kcal/mol) for Conrotatory Ring Closure and Single and Synchronous Double Rotation of the Parent Allyl Anion

	Conrotation	Single rotation	Double rotation
MINDO/3	41	11	67
STO-3G	78	29	133

In the case of the allyl anion **1** a decision can be made by means of the kinetics of the conrotatory ring opening

$$2 \xrightarrow{k^2} 1$$

$k^2_{62°C} = 1.45$ s^{-1}.[1,2] Thus, at 62 °C, ring opening of **2** is ca. 70 times slower than the exchange process. Furthermore, since the equilibrium **2** ⇌ **1** lies far on the side of **1** (**1:2** ≥ 20:1[12]), ring closure of the allyl anion **1** is ≥1400 times slower than topomerization. Therefore, cyclopropyl anion **2** is not an intermediate. The topomerization must occur via bond rotation.

Although it is not known whether this finding corresponds to the general case, the following arguments can be adduced to support the contention that the cyclopropyl anion is by-passed in other cases as well. (a) MINDO/3[13] and STO-3G[14] calculations of the parent allyl anion also favor stepwise single rotation to ring closure (Table I). (b) Electron stabilizing groups at C^2 of the allyl anion should strongly favor topomerization via the cyclopropyl anion. As shown above, this, at least, is not the case with allyl anion **1** bearing a cyano group at C^2. (c) Hydrogen at C^2 of the allyl anion should, on the other hand, prevent topomerization via the cyclopropyl anion because no clearcut example of a 1-H-substituted cyclopropyl anion is known where ring opening occurs.[1,2] Since there exist several 2-H-substituted allyl anions which topomerize,[4,16] the cyclopropyl anion is also not an intermediate in those cases.

(2) The rotation leading to topomerization of **1** is proton catalyzed and proceeds through undetectable concentrations of *trans*-α-benzylcinnamonitrile. This is excluded since no deuterium is incorporated into **1** in Me$_2$SO-d_6 under conditions of fast topomerization.

(3) The gegenion Me$^+$ participates in the topomerization. In that case the rate should depend on the nature of Me$^+$ and the solvent.[4,6,16,17,22] When we measured the NMR spectrum of **1** with Li$^+$, Na$^+$, and K$^+$, respectively, in Me$_2$SO and with Li$^+$ in tetrahydrofuran (THF),[18] not only the chemical shifts in the "low-temperature" spectrum at 5 °C but also the temperature dependence were the same. Therefore, **1** should exist in the ground state as a solvent separated ion pair.[19] Likewise, the rotation reaction should take place in the anion itself as part of the separated ion pair, and not in a less ionic species (i.e., contact ion pair).[19] The transition state is thus well described by **4** with a charge distribution analogous to that of the benzyl anion in a separated ion pair. This is in accordance with observations of Fraenkel, Russel, and Chen[17] who reported that benzyl anions exist as solvent separated ion pairs under comparable conditions.

(4) Since synchronous double rotation directly transforming **1** into **1** as a further possibility is not at all consistent with the small experimental barrier ($\Delta G^{\ddagger}_{62°C} = 16.5$ kcal/mol) and the result of the calculations (Table I), the topomerization must occur by stepwise interchange of substituents at the terminal carbon atoms of **1** via (*Z,Z*)-1,3-diphenyl-2-cyanoallyl anion (**3**) as an intermediate (Scheme I). The existence of the (*Z,Z*)-allyl anion **3** in small concentrations in the presence of **1** is supported by trapping reactions with olefins like acenaphthylene.[1] After protonation two cycloadducts **5** and **6** were isolated in overall 91% yield with phenyl groups at C^7 and C^9 exclusively in cis position (Scheme II).

Scheme II

4   5   6
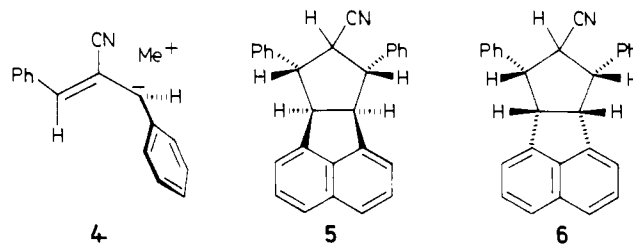
We thus conclude that the topomerization of **1** proceeds via stepwise rotation around the allyl anion bonds and not via cyclopropyl anion **2**,[21] with the gegenion playing no role. Furthermore, one can extrapolate that the cyclopropyl anion should also be by-passed in other cases of allyl anion topomerizations.[4,6,16,20,22]

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(8) The assignment of H^1 and H^3 is based on comparison with the signals in *cis*- and *trans*-α-benzylcinnamonitriles.[1]
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(18) For NMR spectroscopy, 0.25 M solutions of **1** were used, sealed in a tube. Preparation: to *cis,trans*- or *trans,trans*-diphenylcyclopropane-1-carbonitrile[1,2] a solution of lithium (sodium, potassium) methylsulfinylmethide in Me$_2$SO or lithium diisopropylamide in THF, respectively, was added at 0 °C and then allowed to warm.
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(21) Although not mentioned explicitly, a similar mechanism probably applies for the topomerization of the (*Z,E*)-1,3-diphenyl-2-methylallyl anion.[6]
(22) We are grateful to a referee who informed us about the rotational barrier of allylpotassium in THF-d_8 ($\Delta G^{\ddagger}_{60°C} = 17$ kcal/mol), reported by T. B. Thompson and W. T. Ford, Abstracts, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975, Organic Division paper 67. For a comparison of $\Delta G^{\ddagger}$ values it is, of course, important to know the ionic character of allylpotassium, since the rotational barrier of allyllithium in THF amounts only to $E_A = 10.5$ kcal/mol.[16] This demonstrates the strong dependence of the rotational barrier of the gegenion in contact ion pairs

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