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ELECTRON TRANSFER ON *CIS*- AND *TRANS*-1,2-DIPHENYLCYCLOPROPANE: STEREOISOMERIZATION AND FORMATION OF 1,3-DIPHENYLPROPENE AND 1,3-DIPHENYLPROPANE

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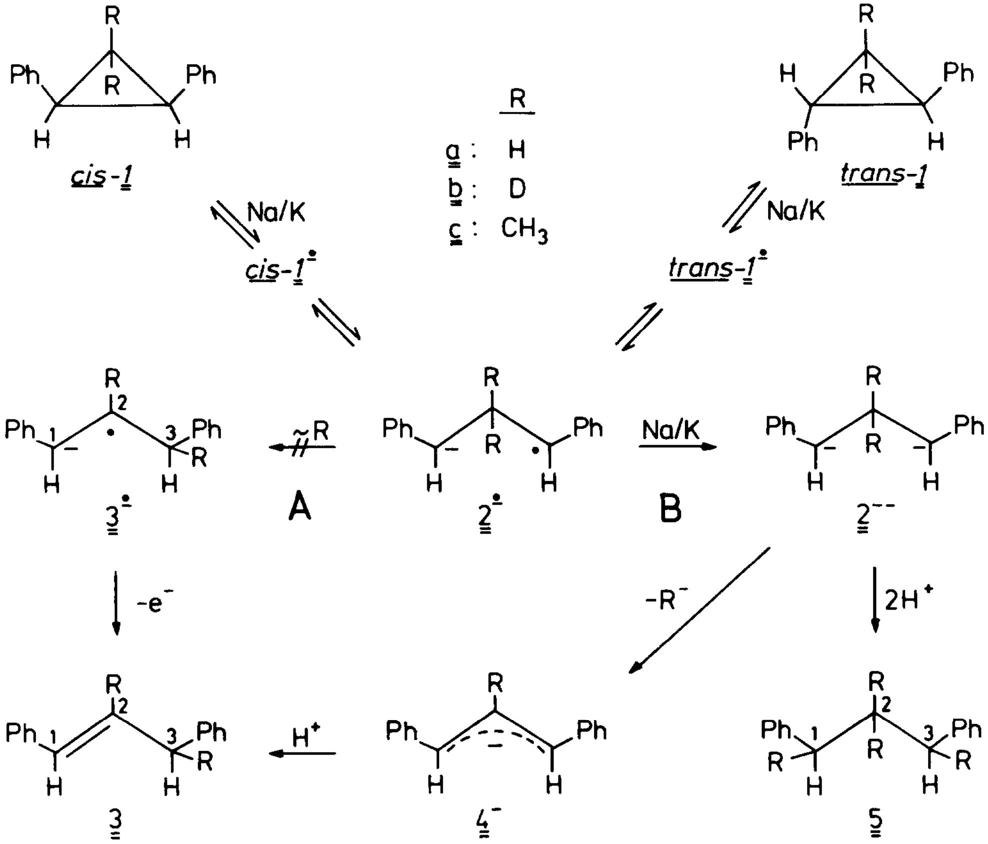
Abstract: Reaction of *cis*- or *trans*-1,2-diphenylcyclopropane with Na/K leads to stereoisomerization and (after protonation) to 1,3-diphenylpropane and 1,3-diphenylpropene, the latter not being formed by H-migration.

Geometrical and structural isomerization of *cis*- and *trans*-1,2-diphenylcyclopropane (*cis*- and *trans*-1a) has been induced by a variety of methods. The thermal reaction between 161 and 220°C results in stereoisomerization and no formation of 1,3-diphenylpropene (3a)[1]. This reaction provides one of the many examples of thermal stereomutations of cyclopropanes via trimethylenes[2]. The activation energy of the *cis* → *trans* isomerization amounts to E_A = 140.2 kJ mol^{-1}, and at equilibrium at 193°C a *trans:cis* ratio of 10:1 pertains[1a]. In the presence of palladium on charcoal at 150°C, however, the geometrical isomer 3a is produced preferentially[3]. In the light induced reaction (2537 Å) stereoisomerization predominates over branching into other products (*cis*- and *trans*-3a; 1-phenylindane) by a ratio of 4:1. Trimethylenes are postulated as common intermediates for the geometrical and structural isomerization[4]. The photosensitized stereoisomerization occurs via the corresponding trimethylene radical cation which is formed by electron transfer from *cis*- and *trans*-1a followed by ring opening[5].

We report on the electron transfer reactions on *cis*- and *trans*-1a with sodium-potassium alloy (Na/K) in tetrahydrofuran (THF). It is shown that stereoisomerization of *cis*- and *trans*-1a and formation of the 1,3-di-"anion" $2a^{--}$ (Scheme I) occur via a common intermediate, the trimethylene radical anion $2a^{\dot{-}}$. The structural isomer 3a, however, is not formed from $2a^{\dot{-}}$ via migration of R(=H), (route A), as suggested earlier for similar cyclopropyl compounds under comparable conditions[6,7]. Rather, route B is the preferred pathway. These conclusions are supported by the reactions of 1b and 1c with Na/K.

The product distributions as a function of time of two characteristic reactions of *cis*- and *trans*-1a with Na/K are given in Tab. 1.

Scheme I: *cis/trans* isomerization of the *cis*- and *trans*-1,2-diphenylcyclopropanes 1a-c and formation of the 1,3-diphenylpropanes 5a-c and 1,3-diphenylpropenes 3a,b with Na/K in THF.



Tab. 1: Relative amounts [%] (vpc analysis) of *cis*-1a, *trans*-1a, 3a (*cis* and *trans* isomer) and 5a in the reactions of a: *cis*-1a[a] and b: *trans*-1a[a] with Na/K[b] in THF (5 ml) at 0°C, followed by protonation with H_2O[c].

	a: *cis*-1a					b: *trans*-1a				
time[min]	0[d]	10	45	120	240	0[e]	10	45	120	240
cis-1a	95	83	8	1	-	4	5	2	2	-
trans-1a	5	5	57	28	9	96	59	28	4	1
3a	-	-	5	30	53	-	2	21	47	71
5a	-	12	30	41	38	-	34	49	47	28

a: 97.0 mg (0.50 mmol) 1a; b: 310 mg (5.0 mmol) Na/K (1:1); c: total yields of *cis*- and *trans*-1a, 3a and 5a: 90-100%; d: *cis*-1a contained 5% *trans*-1a; e: *trans*-1a contained 4% *cis*-1a.

The data given in Tab. 1a can be summarized as follows: 1. *cis*-1a disappears steadily; 2. the concentrations of *trans*-1a and 5a pass through a maximum which demonstrates the intermediate nature of *trans*-1a and 2a^{--} (2a^{--} gives 5a on protonation, as confirmed by deuteration); 3. 3a (resulting from 4a^{-} on protonation, again confirmed by deuteration) increases steadily.

Starting from the thermodynamically more stable isomer *trans*-1a leads to a comparable result: *trans*-1a disappears steadily while 5a goes through a concentration maximum; *cis*-1a is formed only in minor concentration.

These results indicate that the reactions of *cis*- and *trans*-1a with Na/K occur as outlined in Scheme I: Initial electron transfer gives via *cis*- and *trans*-1a$^{\dot{-}}$ the trimethylene radical anion 2a$^{\dot{-}}$ and thus the intermediate for a facile stereoisomerization. The thermal *cis* → *trans* isomerization of *cis*-1a at 22°C is extrapolated to have a half-life of $8\cdot10^{8}$ years(!)[1a]. Furthermore, in competition with the reversible formation of 2a$^{\dot{-}}$, this species is trapped by Na/K to give the di-"anion" 2a^{--}[8], which is the only intermediate to give 4a^{-}: via elimination of hydride (route B).

The facile formation of 4a^{-} from 2a^{--} is demonstrated also if *cis*- or *trans*-1a are reacted with excess lithium at -60°C[9]. Protonation of the orange solution after 3 h at -60°C leads to 5a. Warming the orange solution to room temperature results in a colour change to deep purple; protonation of this solution results in 3a. At the same time evolution of H_2 is observed.

When the bis-deuterated *trans*-1b was reacted with Na/K in THF at 0°C one observed on protonation after 1 h 16% *trans*-1b, 6% 3b (R^2=D,R^3=H) and 78% 5b (R^2,$R^{2\prime}$=D;R^1,R^3=H). Most importantly, the propene 3b (R^2=D;R^3=H) contained only one deuterium atom , while the propane 5b (R^2,$R^{2\prime}$=D; R^1,R^3=H) had two[10]. It is thus unambigously clear that 3b (R^2=D;R^3=H) is formed from 2b^{--} by loss of D^{-} to give 4b^{-}, followed by protonation of 4b^{-} [11] (route B). Route A - deuterium migration 2b$^{\dot{-}}$ → 3b$^{\dot{-}}$ (R^2,R^3=D), followed by loss of an electron to give 3b (R^2,R^3=D) - is not a viable process.

Literature data are in agreement with the observations in the case of 1a and 1b: the intramolecular 1,2-migration of hydrogen (deuterium) is not a facile reaction in either radicals[12] or carbanions[13].

Intermolecular H(D)-migration is also excluded since the eliminated D^{-} does not show up in any of the products examined.

The reactions of the bis-methylated *cis*- and *trans*-1c with Na/K nicely confirm the results with 1a,b. For example, *cis*-1c gives on protonation after 25 min at 23°C 0% *cis*-1c, 58% *trans*-1c and 42% 5c (R^2,$R^{2\prime}$=CH_3;R^1,R^3=H); after 3 h, *trans*-1c has also disappeared almost completely (2%) at the cost of 5c (R^2,$R^{2\prime}$=CH_3; R^1,R^3=H). At -78°C from *cis*-1c only small amounts (a maximum of 4% after 45 min) of *trans*-1c are formed besides 5c (R^2,$R^{2\prime}$=CH_3;R^1,R^3=H). Ring closure of the intermediate trimethylene radical anion 2c$^{\dot{-}}$ to the thermodynamically more stable *trans*-1c at that temperature apparently is much more unfavourable than further reduction, probably due to steric hindrance. Significantly, a propene has never been observed in the reactions of *cis*- as well as *trans*-1c with Na/K! Its formation would require the migration (elimination) of a methyl group in 2c$^{\dot{-}}$ (2c^{--}) which has no precedence in comparable species.

Finally, it should be noted that 1,3-di-"anions" like 2^{--} are of current theoretical interest[14]. In agreement with calculations[14], 2a(b)$^{--}$ loses easily H^{-}(D^{-}). More importantly,

$2c^{--}$ is a stable 1,3-di-"anion" thus possibly allowing to verify experimentally the prediction of the double lithium bridged structure of the corresponding 1,3-dilithiopropane.

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