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# PREPARATION OF AND DYNAMIC GEARING IN *CIS*-1,2-BIS(9-TRIPTYCYL)ETHYLENE[1]

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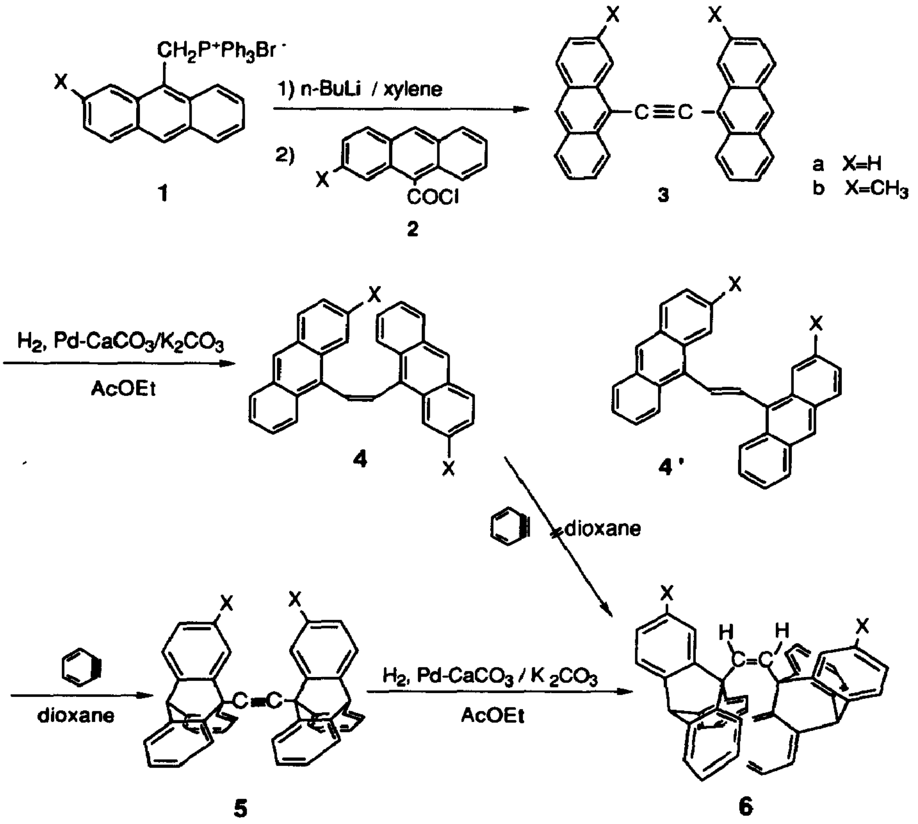
*Summary*: The two tortional degrees of freedom about the bond from the bridgehead to the olefinic carbons in *cis*-1,2-bis(9-triptycyl)ethylene couple slightly less strongly than those in the corresponding methane in spite of the apparently deeper meshing of the two triptycyl moiety, which manifests itself in the unusually large nuclear spin-spin coupling between the olefinic protons.

Dynamic gearing in bis(9-triptycyl)X type molecules have been under scrutiny over a decade by us and Mislow's group[3] at Princeton. The barrier heights for gear slipping( $\Delta H^{\ddagger}$ ) as measured by the interconversion of the *meso* and *dl* isomers of the 2-chloro derivatives are markedly dependent on the joint group X ( $CH_2$, NH, O, $SiH_2$, PH, S, Se ), and range from as low as 20.4 kcal/mol of the silane[4] to as high as 41.0 kcal/mol of the ether.

In the molecules previously studied by us, the two concerned bonds extending from the bridgehead carbons meet at a single atom. Our next interest is adding another atom to connect the bridgehead carbons of two 9-triptycyl moiety by three consecutive bonds. Because the angle and/or distance between the two 9-triptycyl groups are expected to be considerably different from those of the previous studies, tightness of the gearing in these systems is difficult to predict and remains to be determined experimentally. The candidates for the central bond include a *cis*-vinylene group either isolated or incorporated into a small-membered carbocycle and *cis*-1,2-cycloalkanediyl of small ring size. It is also to be noted that if the gearing in these molecules are tight enough, these system can be extended to a cyclic multiply correlated system, where even or odd multiplicity gives rise to a completely different internal motion. Tris(9-triptycyl)cyclopropenylium perchlorate recently described by Mislow *et al.*[6] is the first example of triply correlated system connected by a bond having an intermediate nature between single and double bond. Here we report the preparation of *cis*-1,2-bis(9-triptycyl)ethylenes, the separation of the phase isomers of an ethylene with labeled vanes , and the kinetics of their interconversion.

The ethylenes **6** were prepared according to scheme 1. In the early stage we tried to get unlabeled ethylene **6a** through addition of benzyne to *cis*-1,2-bis(9-anthryl)ethylene **4a**,[7] which has been known and is easily obtainable by catalytic hydrogenation of bis(9-anthryl)acetylene **3a**.[8] However the acetylene **3a** obtained through Wittig reaction of 9-anthrylmethylidentriphenylphosphorane **1a** with 9-anthracenecarbonyl chloride **2a** was always contaminated by *trans*-1,2-bis(9-anthryl)ethylene **4a'**,[9] which could not be cleared after all efforts. Naturally hydrogenation of the impure **3a** gave *cis*-ethylene **4a** contaminated by the *trans* isomer, which again could not be removed due to the much lower solubility compared to the *cis* counterpart. More fatal is the rapid isomerization of the *cis* - to the *trans*-ethylene under the standard conditions of benzyne generation ( anthranilic acid and isopentyl nitrite in *p*-dioxane, 50~60°C ). Seemingly *cis*-1,2-bis(9-

**scheme 1**

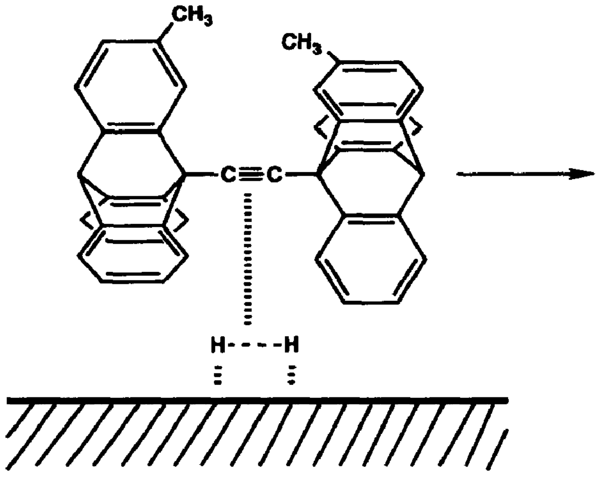


anthryl)ethylene **4a** is susceptible to attack by a radical to give a resonance-stabilized anthrylmethyl radical. Rotation about the concerned C-C bond followed by loss of the added radical will give the thermodynamically more stable *trans* isomer **4a'**.

Addition of benzyne to the acetylene **3a** ( *vied supra* ) and hydrogenation of the resultant bis(9-triptycyl)acetylene **5a** to *cis*-1,2-bis(9-triptycyl)ethylene **6a** have resulted in limited success in spite of various attempts mainly due to the low solubility of the acetylene. Small amount of the target molecule was obtained after laborious purification procedures.

Substituted ethylenes were prepared in a similar manner. In the previous studies chlorine atom has been introduced at C-2 of 9-triptycyl group to give rise to moderate differences in physical properties between the *meso* and *dl* isomers(*vide supra*). However even under the mildest hydrogenation conditions used (Lindlar catalyst, 1 atm $H_2$, ambient temp. ), the chlorine did not survive. Thus methyl substituent was adapted and the *meso* and *dl* isomers of **6b** were separated by hplc.

Most interesting feature of the hydrogenation of bis(2-methyl-9-triptycyl)acetylene **5b** is a high stereoselectivity to give the *dl* isomer of *cis*-1,2-bis (2-methyl-9-triptycyl)ethylene **6b** ( *dl / meso* = *ca.* 9 / 1 ). This preference is apparently explicable by simple steric reasons( Fig 1 ). **5b** is hydrogenated in such a conformation as to avoid the interaction of the methyl-substituted benzene rings with the catalyst surface.



*dl*-**6b**

Fig.1 Hydrogenation of the acetylene **5b** on the catalyst surface

Kinetics of the interconversion of the *meso* and *dl* isomers of **6b** was carried out by following the change either of the signals due to the methyl protons by nmr or of the absorbance at 254 nm by hplc on a solution in benzene-$d_6$. The ethylene ( activation parameters for the *dl* to *meso* isomerization: $\Delta H^\ddagger = 30.0 \pm 0.2$ kcal/mol $\Delta S^\ddagger = -3.7 \pm 0.4$ e.u.) isomerizes a little faster than the corresponding methane( $\Delta H^\ddagger = 31.1 \pm 0.4$ kcal/mol $\Delta S^\ddagger = -6.9 \pm 0.9$ e.u.).[10]

Combined use of the standard bond lengths($Csp^3$-$Csp^3$ = 1.526 Å, $Csp^2$-$Csp^2$ = 1.335 Å, $Csp^2$-$Csp^3$ = 1.510 Å ), angles( $sp^2$ = 120°, $sp^3$ = 109.5° ), and the results of the X-ray structural analysis of triptycene or its derivative[11] gives the longer distances between the two bridgehead carbons for the ethylene ( about 2.9 *vs.* 2.5 Å ). However this longer distance is offset by much smaller angle( 60° *vs.* 109.5° ) and the inside one of the two benzene rings coplanar with the double bond in a $C_s$ conformation is tucked much more deeply into the notch of the other 9-triptycyl moiety. The ethylene would have the larger barrier for the gear slippage without an extensive perturbation to the structure to reduce the nonbonded repulsion. In fact, large deviations of the molecular dimensions from the standard values have been noted whenever studied in bis(9-triptycyl)X type molecules.[12] It is inferred that with an extra intervening bond, the ethylene is structurally more flexible and relaxes the steric congestion more effectively, especially in the transition state for the gear slippage. In this regard, the barrier height of ca.19 kcal/mol ( $\Delta G^\ddagger$ at coalescence temperature) for bis(9-triptycyl)cyclopropenone,[6] which has a formal double bond but whose two axes of the 9-triptycyl groups made much larger angle, is impressively small.

The more severe overcrowding of the ethylene as compared to the corresponding methane in the ground state manifests itself in the nmr spectra. Nuclear spin-spin couplings found in the *cis*-1,2-bis(9-triptycyl)ethylenes are rather unusual. $^3J_{HH}$ obtained from the $^{13}C$ satellite peaks for the olefinic protons of **6a** is 16.3 Hz and considerably larger compared to normal values of 6~12 Hz. In sharp contrast, $^3J_{HH}$ for the *trans* compound as is inferred from the AB quartet due to the olefinic protons of *trans*-1-(9-triptycyl)-2-(2-methyl-9-triptycyl)ethylene is quite normal ( 17.8 Hz).[13] It is well known $^3J_{HH}$ of cyclic olefins increases with ring size and reaches the constant value of ca.12.5 Hz and the increase is ascribed to the decrease in the

C=C-H angle.[14] In the present case, severe congestion in the cis isomer may cause increase of the C=C-C and concomitant decrease of the C=C-H angles.

The chemical shifts of the protons spread more widely compared to the corresponding methane. For example, the methyl signals of **6b** appear at 1.58 ( *meso* ) and 1.06 ( *dl* ) ppm, whereas those of the methane are found at 1.86 and 2.04 ppm,respectively. To the contrary, the signals due to the 1-, 8-, and 15-H appear lower fields. It is quite possible that ring current effects to cause highfield shift and/or van der Waals shifts to lower field are larger in the case of ethylene.

Detailed structural studies are in progress.

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9) This observation hasn't been mentioned by the original authors. **4a'** is considered to be produced through Wittig reaction with 9-anthraldehyde formed by the oxidation of **1a** under the rather severe reaction conditions( xylene reflux ).
10) Unpublished results.
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13) In the case of the unsubstituted *trans*-ethylene **6a**, only the $^{13}C$ satellite peaks at the low-field side are discernible for the olefinic protons. It is difficult, however, to get accurate $^{3}J_{HH}$ values based only on these signals.
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