CHEMISTRY LETTERS, pp. 209-212, 1980. © The Chemical Society of Japan 1980

A SURPRISING DIFFERENCE IN REACTIVITIES OF 1,2,3,4-TETRACHLORO-9-(2-CHLORO-1,1-DIMETHYLETHYL)TRIPTYCENE ROTAMERS. A REACTION CATALYZED BY LEWIS ACIDS[1]

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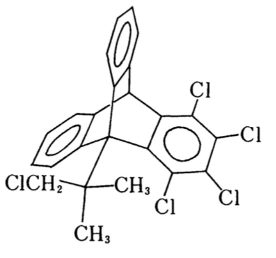
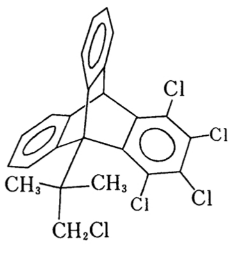
±sc-1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene was found to react in the presence of $TiCl_4$ at room temperature, whereas the ap isomer required $SbCl_5$ to react. Both gave practically the same mixture of 1,2-dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylenes. The structures of the products were confirmed by independent syntheses.

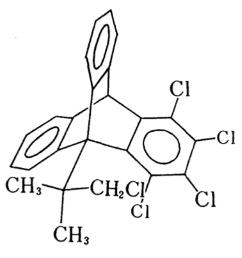
Reactivities of rotamers have been variously discussed. Classical considerations of Curtin-Hammett,[2] Winstein-Holness,[3] and Eliel-Ro[4] were mathematically treated.[5] However, the necessity of obtaining information about the reactivities of rotamers still stands for better understanding of the reactivities of organic compounds. There are a few examples which exhibit the difference in reactivities of rotamers involving a C_{sp^3}-C_{sp^2} bond. After the isolation of stable rotamers,[6] we have been able to show that the rates of lithiation of 9-arylfluorene derivatives can differ by a factor of 1,000 in two rotameric forms.[7] Dubois et al. have demonstrated that the rotameric forms of di-tert-butyl(o-methylphenyl)carbinols exhibit different reactivities.[8] We wish to reveal in this communication that rotamers of the ethane type can show surprisingly different reactivities in cationic reactions.



(*ap*-1)

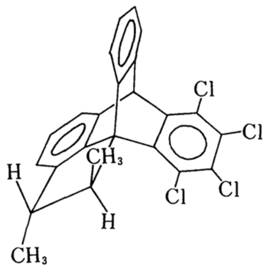


(−*sc*-1)

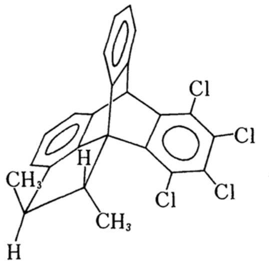


(+*sc*-1)

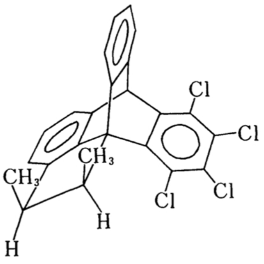
The first indication of the difference came from chromatographic behaviors of the rotamers of 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (1). Its ap isomer was eluted normally from an alumina column but the ±sc isomer could not survive under the conditions.[1] Alumina might be acting as a Lewis acid. Then we treated a mixture of both isomers in benzene with a weak Lewis acid, $TiCl_4$,[9] at room temperature. After 20 h, a ^1H NMR spectrum showed that the ±sc isomer was completely destroyed but the ap isomer was not affected at all. One product crystallized out from the reaction mixture. Its ^1H NMR spectrum showed the presence of two methyl groups, each of which coupled with a proton, and its mass spectrum showed molecular ions of m/e 452, 450, 448, 446, and 444 which were indicative of the loss of a HCl molecule from the starting material. The results suggest that an isomer of 1,2-dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene (2) is formed.



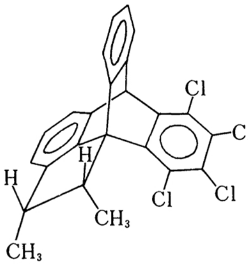
(*trans*-**2a**)



(*trans*-**2b**)

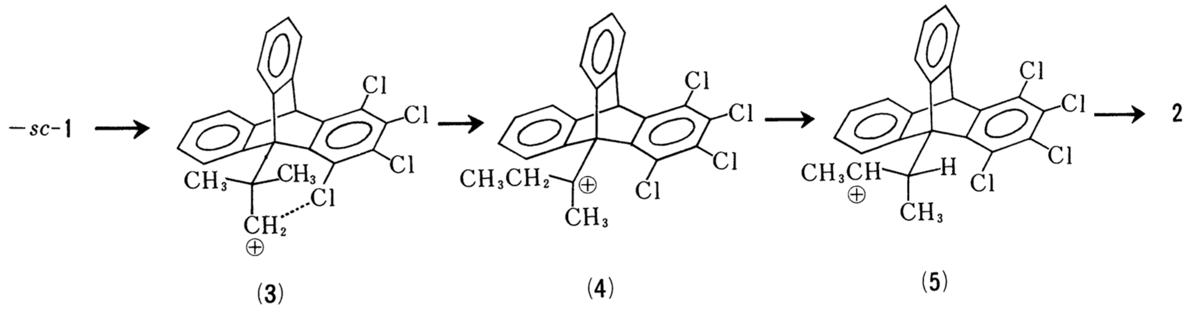


(*cis*-**2a**)

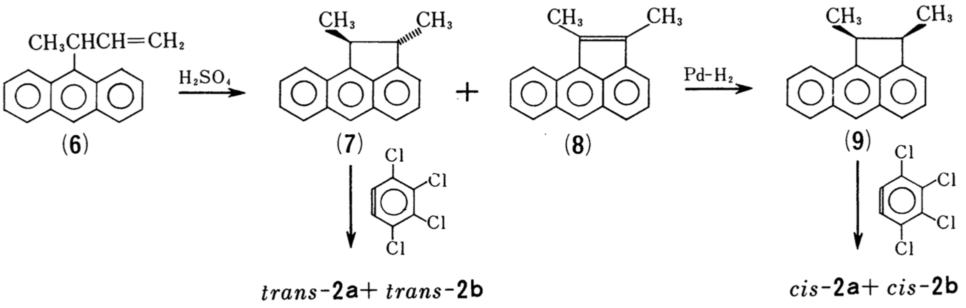


(*cis*-**2b**)

The formation of 2 is mechanistically rationalized by assuming that a carbonium ion is formed by the action of $TiCl_4$, a series of Wagner-Meerwein rearrangements take place, and cyclization ensues: the reaction mechanisms are roughly given in the following scheme.[10]



Thus we decided to synthesize the stereoisomers of 2 by independent paths. 9-(α-Methylallyl)anthracene (6)[11] was treated with concentrated sulfuric acid in CCl_4 at room temperature to give a mixture of cis- and trans-1,2-dimethylaceanthrene (7) and a dehydrogenated product, 1,2-dimethylaceanthrylene (8).[12] The olefin 8, mp 113.0-113.5 °C, was separated and hydrogenated over palladium-carbon to afford cis-1,2-dimethylaceanthrene (9), mp 79-80 °C: ^{1}H MNR ($CDCl_3$), δ 1.26 (3H, d), 1.45 (3H, d), 3.77 (1H, m), 4.11 (1H, m), 7.0-8.2 (7H, m), 8.09 (1H, s). Treating 9 with tetrachlorobenzyne[13] in dichloromethane afforded a mixture of two isomers,



cis-2a and cis-2b, from which a major product was isolated as crystals (mp 272.5-274.5 °C: ^{1}H NMR ($CDCl_3$), δ 1.40 (3H, d), 1.55 (3H, d), 3.35 (1H, m), 3.83 (1H, m), 5.93 (1H, s), 6.8-7.6 (7H, m)) and the other isomer as a solution by HPLC (^{1}H NMR accumulated for 500 times ($CDCl_3$): δ 1.12 (3H, d), 2.11 (3H, d), 3.63 (1H, quintet), 4.48 (1H, quintet), 6.02 (1H, s), 6.8-7.5 (6H, m), 7.87 (1H, m)).

The peri-protons in proximity of the 9-substituent in triptycene derivatives are known to give rise to low field signals in the aromatic region of the ^1H NMR spectra.[14] In the structure of cis-2a, there is a peri-proton which is very close to a methyl group, whereas cis-2b has no such a peri-proton. The ^1H NMR spectrum of the minor product was indicative of the structure cis-2a. In addition the minor product showed the NOE enhancement of the proton signal at the lowest field by 23% on irradiation of the methyl signal at the lower field. The enhancement was not observed with the major product. Then the major product must be cis-2b and the minor cis-2a.

Similarly the crude 7 (^1H NMR ($CDCl_3$): δ 1.29 (3H, d), 1.42 (3H, d), 3.18 (1H, m), 3.59 (1H, m), 6.9-8.2 (7H, m), 8.10 (1H, s)) afforded two products, one of which was obtained as crystals, mp 265.0-266.0 °C: ^1H NMR ($CDCl_3$), δ 1.50 (3H, d), 2.19 (3H, d), 3.21 (1H, m), 3.83 (1H, m), 5.97 (1H, s), 6.8-7.5 (6H, m), 7.90 (1H, m), A NOE experiment with the crystallized product showed 19% enhancement of the aromatic proton signal at the lowest field on irradiation of the lower methyl signal. Therefore the crystallized product is trans-2a and the other trans-2b.[15]

Having established the structures of the products 2, we now analyze the formation ratio of the trans-2a, trans-2b, cis-2a, and cis-2b as ca. 45:~0:10:45. The crystalline product obtained from the original reaction mixture was cis-2b.

ap-1 reacted in the presence of a stronger Lewis acid, $SbCl_5$,[9c,16] although it did not react by the $TiCl_4$ catalysis to a measurable extent after 150 h at room temperature. The products were the isomers of 2 and a small amount of others. The formation ratio of the isomers of 2 was similar with that derived from the ±sc isomer as far as the ^1H NMR spectrum could detect. The similar distribution of the products for the two reactions may mean that a common intermediate exists. Since ap-1 and ±sc-1 are rotational isomers with each other, the most reasonable assumption is that internal rotation takes place in an intermediate. The intermediate may neither be 3 nor 5 since these should possess high barriers to rotation.[17] Rather 4 is a likely intermediate in which internal rotation occurs, because 9-aryltriptycenes are known to possess rather low barriers to rotation.[18]

The surprisingly enhanced reactivity of ±sc-1 must be attributed to the neighboring participation of the chloro group in the peri-position, because numerous examples of chloronium ions are now known.[19] The present data suggest that the reactivities of rotamers may be different by a large factor if there is a group which stabilizes a forming cation in proximity. Other examples of this sort is under investigation.

We gratefully acknowledge the receipt of a grant from Toray Science Foundation which supported this work.

References and Notes

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10) The intervention of an olefin, which is formed by deprotonation of the cationic species, cannot be ruled out at present.
11) This compound was prepared by the Grignard reaction of anthrone with trans-2-butenyl chloride followed by dehydration. ^{1}H NMR data were satisfactory: δ 1.75 (3H, d), 5.00 (1H, m), 5.11 (1H, m), 5.28 (1H, m), 6.41 (1H, m), 7.28-8.6 (8H, m), 8.34 (1H, s).
12) 7 was a major product. 8 increases, at the expense of 7, indicating that sulfuric acid is acting as a dehydrogenating agent.
13) Tetrachlorobenzyne was generated by the action of isopentyl nitrite on tetrachloroanthranilic acid.
14) Since 9-substituted triptycenes are highly congested, strong van der Waals interactions are due between the 9-substituent and the peri-protons in close proximity. From accumulated data of these compounds, it is possible to diagnose the presence and even to count the number of the peri-proton(s) which is close to a tert-alkyl group in 9-position.
15) trans-2b composed ca. 55% of the isomer mixture of the product but has not yet been obtained in a pure form. Following ^{1}H NMR data were obtained by subtracting the signals due to trans-2a from those of the mixture of trans-2a and trans-2b ($CDCl_3$): δ 1.40 (3H, d), 2.00 (3H, d), 2.9-4.2 (2H, m), 6.05 (1H, s), 6.8-7.7 (7H, m).
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(Received December 17, 1979)