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AN INTRAMOLECULAR FRIEDEL-CRAFTS ACYLATION OF ROTAMERIC 9-(2-CARBOXY-1,1-DIMETHYLETHYL)-1,4-DIMETHYLTRIPTYCENE[1)]

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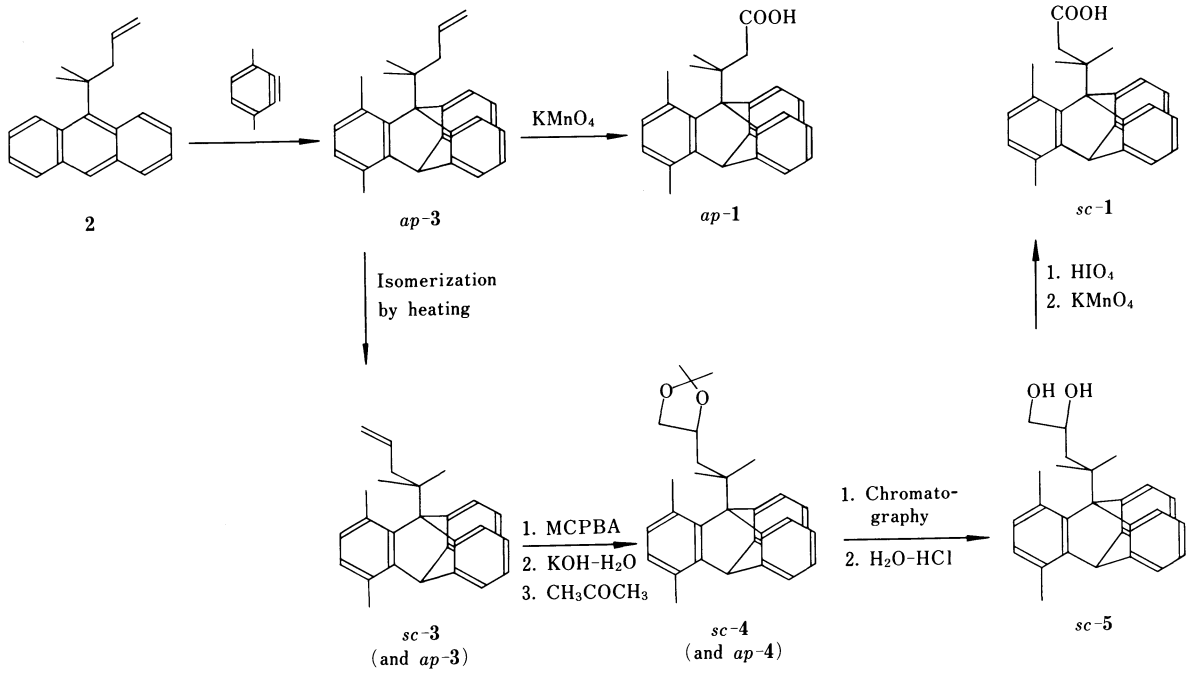
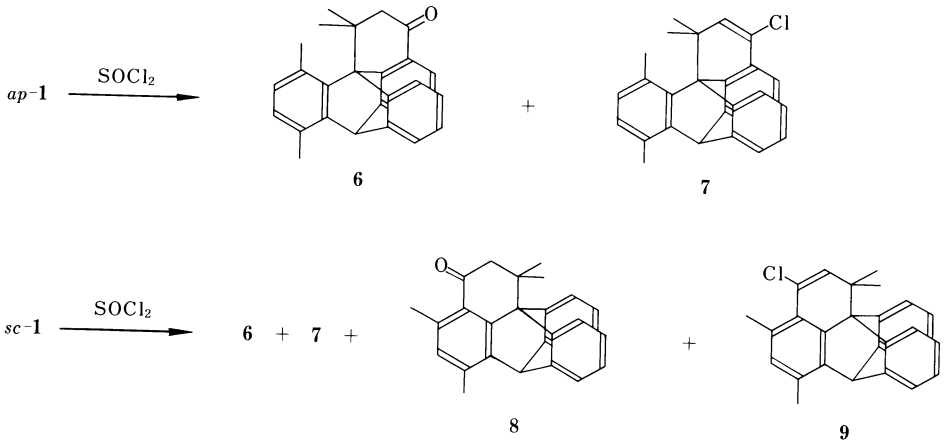
While the ap form of the title compound, on being heated with thionyl chloride, afforded 3-oxo-1,1,8,11-tetramethyl-2,3,7,11b-tetrahydro-7,11b-o-benzenobenzo[j]phenalene and 3-chloro-1,1,8,11-tetramethyl-7,11b-dihydro-7,11b-o-benzenobenzo[j]phenalene, the sc-isomer did, in addition to the above products, those derived from the ipso attack of the intervening acyl cation on the 1-position, the methyl group at the position undergoing the 1,2-shift.

9-Substituted triptycenes comprise an interesting series of compounds because the ground state is congested.[2)] Due to the proximity of two groups in the 1- and 9-positions, unusual interactions are often uncovered between them,[3)] which often lead to intramolecular reactions[4)] or enhancement of reaction rates.[5)] During the course of the series of investigations, we synthesized ap- and ±sc-9-(2-carboxy-1,1-dimethylethyl)-1,4-dimethyltriptycene (1) by the method shown below.



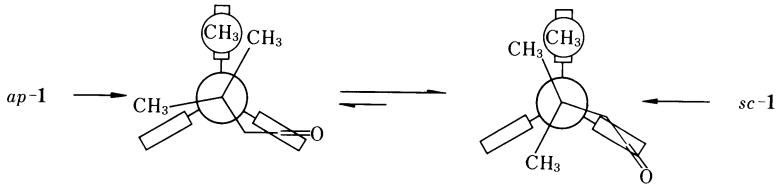
Addition of 3,6-dimethylbenzyne to 9-(1,1-dimethyl-3-butenyl)anthracene (2) yielded ap-1,4-dimethyl-9-(1,1-dimethyl-3-butenyl)triptycene (ap-3) as a main product. Oxidation of ap-3 with potassium permanganate smoothly afforded ap-1.[6] When ap-3 in 1-chloronaphthalene was heated at the boiling point of nitrobenzene for 16 h, it became a mixture of ap-3 and ±sc-3, the sc/ap ratio being 0.69. The rotameric mixture of ap-3 and ±sc-3 was converted to an epoxide by m-chloroperoxybenzoic acid and the product was treated with potassium hydroxide to afford the corresponding diol (5) which was then derived to a mixture of acetonides (4). Chromatographic separation was possible at this stage, ±sc-4 and ap-4. Although diastereomers exist in ±sc-4 due to the presence of a chiral center in the 9-substituent, those are not separable by chromatography. ±sc-4 is then deprotected to produce ±sc-5 which was oxidized to the corresponding aldehyde with periodic acid and then to ±sc-1[6] with potassium permanganate. This lengthy way of preparation of ±sc-1 was necessary because attempts at separating the rotamers at various stages other than 4 were not successful.

When the carboxylic acid (1) was heated with excess of thionyl chloride for 2.5 h, it did not give the expected acid chloride but afforded other compounds: the ap form afforded two products, whereas the sc form did four. There is a precedence of this type of reactions: 3-(9-triptycyl)propionic acid affords a cyclic ketone on heating with thionyl chloride.[7] The spectral features of one of the products from ap-1 were consistent with the proposed ketone structure (6) which should be obtained by simple intramolecular Friedel-Crafts acylation: presence of a carbonyl band in IR spectrum, presence of diastereotopic methylene protons, and loss of one aromatic proton from the parent compound in ^{1}H NMR spectrum.[8] The other product lacks a carbonyl group but possesses an olefinic proton.[9] Mass spectrum indicates that a chlorine atom is present in the product.[9] Furthermore, the same type of reactions could be caused by heating ap-1 with oxalyl chloride in benzene, but it produced a sole product, the ketone 6, this time. Thus it was suspected that the once-formed ketone underwent further reaction with thionyl chloride to produce the chloro compound. Indeed, treating the ketone 6 with thionyl chloride produced the second product. Easily enolizable ketones such as 1,3-diketones[10] and acetophenone[11] are known to produce chloro-olefins under the



similar conditions. These considerations lead to the structural assignment of the second product to the chloro olefin 7. The spectral data are consistent with the proposed structure.

Of the four products from ±sc-1, two were identical with 6 and 7 obtained from ap-1. A simple consideration of the reaction rationalizes the formation of 6 and 7 from both ap-1 and ±sc-1: whereas there are two identical benzeno bridges in ap-1 with which the Friedel-Crafts acylation is to occur, there is one benzeno bridge in ±sc-1 which should give the same product 6 if the reaction occurs there. However, there is a point which is worthwhile to consider in depth. Namely, the ketone 6 can take two conformations, 6a and 6b, which are exactly formed from the ap and sc forms, respectively. If passing of the methyl groups over the benzeno bridges is difficult as is in other 9-t-alkyltriptycenes, these isomers, 6a and 6b, must be recognized as stable entities. Since we find only one compound in ^{1}H NMR spectrum, the rusults mean that either the equilibrium between 6a and 6b is attained very rapidly or one conformer is too unstable to be detected. In order to clarify this point, we carried out the MM2 calculation to obtain steric energies of these conformers. The results indicate that 6b is 5.2 kcal/mol more stable than 6a. Thus we conclude that only conformation 6b is observed. During the cyclization reaction, it seems that the 6-membered ring takes the lopsidedly stable conformation.



6a 6b

Two products from ±sc-1 other than 6 and 7 are naturally considered to be derived by the Friedel-Crafts acylation of another benzene ring which bears the methyl groups. In this case, however, because of the structural requirement, the attack of the acyl cation must occur at the ipso position[13] where one of the methyl groups has been present. Then the fate of the methyl group and/or the acyl group is of interest. ^{1}H NMR spectrum of one of the products which shows the C=O absorption in IR spectrum indicates that two aromatic methyl groups are still present but there is only one aromatic proton which gives a signal at a high field.[12] Since the starting material shows the presence of two such protons, these must be assigned to the protons which are attached to the aromatic ring with two methyl groups. This strongly indicates that, after the ipso attack by the acyl cation, the methide migration takes place, which is then followed by deprotonation, to result in the formation of 8. Treatment of the ketone 8 with thionyl chloride afforded a product which was identical with another.[14] Thus the latter compound is assigned to structure 9.

Summarizing the rusults, we come to the following conclusion. Whereas the ap form affords a normal Friedel-Crafts acylation product becuase of the fact that there are two identical benzene rings that bear no substituent at the site of the

reaction, the sc form affords products which are derived by the attacks of the acyl cation on two different benzene rings. The methyl group originally located at the point of the ipso attack undergoes a 1,2-shift to form a rearranged product. Thus this work provides another example in which rotational isomers give different products under identical conditions.[15)]

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9) ^{1}H NMR data of 7 ($CDCl_3$, δ): 1.72 (3H, s), 2.20 (3H, s), 2.33 (3H, s), 2.54 (3H, s), 5.51 (1H, s), 6.37 (1H, s), 6.49 and 6.55 (2H, ABq, J=8 Hz), 6.8-7.3 (5H, m), 7.35-7.5 (1H, m), 7.7-7.9 (1H, m). EI MS data of 7: M^+ 382, 384.
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13) ^{1}H NMR data of 9 ($CDCl_3$, δ): 1.73 (3H, s), 2.11 (3H, s), 2.43 (3H, s), 2.46 (3H, s), 5.41 (1H, s), 6.40 (1H, s), 6.63 (1H, br s), 6.7-6.8 (2H, m), 7.0-7.3 (3H, m), 7.4-7.6 (2H, m), 7.7-7.9 (1H, m). EI MS data of 9: M^+ 382, 384.
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