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Strong Participation of the 1-Methyl Group in Diazotization Reaction of 9-Aminomethyl-1,4-dimethyltriptycene

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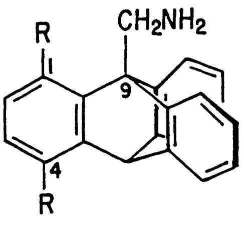
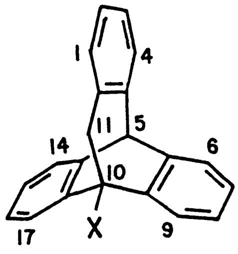
The title reaction in acetic acid gave 5-methyl-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene and 1-acetoxymethyl-4,9-dimethyltriptycene as major products and only small amounts of skeletally rearranged homotriptycene derivatives to indicate strong participation of the peri-methyl group in the reaction.

Insertion of a carbocationic species into an aliphatic C-H bond is of great interest in organic chemistry both theoretically and experimentally. Several examples indicative of such a process have been reported but they seem to be limited to special cases: 1) reactions in the gas-phase such as $CH_3^+ + CH_4 \longrightarrow C_2H_7^+$ have been studied,[1)] 2) carbocations produced in super acids insert into a C-H bond to form pentacoordinated species,[2)] 3) formation of cyclopropanes that results from intramolecular γ-C-H insertion of appropriate carbocations is known both *in vitro*[3)] and *in vivo*,[4)] and 4) formation of four-membered and larger rings is completely unknown except the formation of a cyclobutane ring in a highly congested cage compound.[5)] The last example suggests that close proximity of the cationic center and the C-H bond is a prerequisite for the insertion. Based on our long experience in triptycene chemistry, we expected that, if a carbocation is produced at the α-position of a bridgehead substituent and there is a methyl group at one of the *peri*-positions of the triptycene skeleton, they would strongly interact with each other, since the distance involved is very short (*ca*. 3.0 Å[6)]), and that there might be a chance to afford C-H insertion products.

We report here the results of diazotization reaction of 9-aminomethyl-1,4-dimethyltriptycene (**2**) which was shown to meet our expectation. Cristol and Pennelle reported that the reaction of the parent 9-aminomethyltriptycene (**1**) with nitrous acid in acetic acid leads to extensive skeletal rearrangement affording 10-hydroxy-10,11-dihydro-5,10-o-benzeno-5H-dibenzo[a,d]cycloheptene (**3a**: 42%) (hereafter referred to as 10-hydroxyhomotriptycene) and its acetate (**3b**: 56%).[7)] The plausible driving force for the skeletal rearrangement



1 R=H
2 R=CH_3

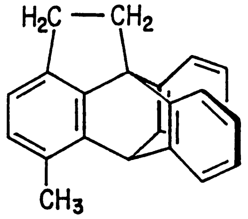


3a X=OH
3b X=$OCOCH_3$

should be the inherent strain of the triptycene skeleton: our molecular mechanics calculation showed that 9-methyltriptycene is more strained than the isomeric homotriptycene by 5.6 kcal/mol. Our results presented here indicate that the presence of the <u>peri</u>-methyl group in the triptycene skeleton strongly prefers the C-H insertion to the otherwise energetically favored skeletal rearrangement.

The synthesis of 2 was carried out as follows. 9-Anthracenecarboxaldehyde was converted to its acetal with ethylene glycol and the acetal was treated with 3,6-dimethylbenzyne to produce the corresponding triptycene. Deacetalization, oxime formation, and reduction with lithium tetrahydridoaluminate afforded the desired compound in the overall yield of 22%.8) The amine **2** was converted to its hydrochloride and the salt was treated in acetic acid with 10 equivalents of sodium nitrite at room temperature for 15 h. Preparative gel permeation chromatography gave five isolated products **4**-**8** (Table 1). The plausible mechanistic pathways to the products are shown in Scheme 1.

Although the mechanism of nitrous-acid deamination of aliphatic primary amines is still controversial in the details,9) general consensus is that the rate-determining step is the formation of a nitrosoamine which isomerizes to a diazonium salt in the presence of acid, the diazonium salt rapidly losing nitrogen



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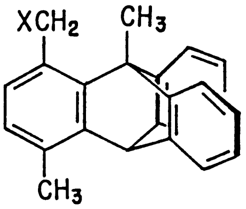
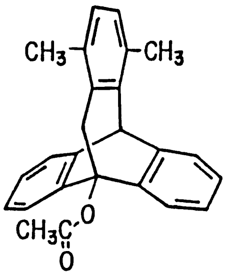


5 X = OCOCH$_3$
6 X = Cl



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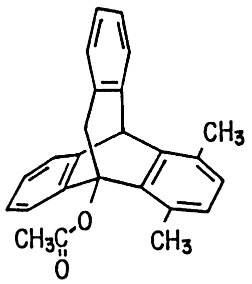

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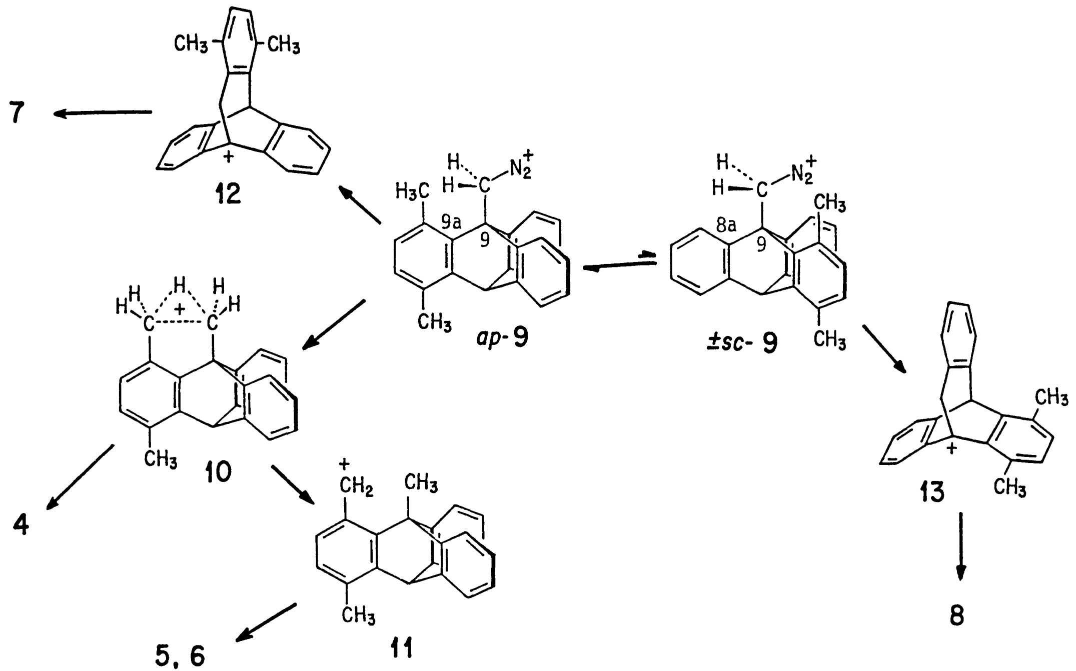
Table 1. Yields, mp,and spectral data of the products

4	46%; 243-245 °C; ms: m/z 294(M^+,100%), 279(80%); δ(H): 2.380(3H, s), 3.15-3.35(4H, m), 5.571(1H, s), 6.757(2H, s), 6.90-7.04(4H, m), 7.34-7.40(4H, m); δ(C): 17.20q, 23.05t, 32.77t, 51.12d, 60.16s, 120.40d, 120.94d, 123.94d, 124.50d, 124.74d, 127.78d, 129.44s, 133.92s, 139.92s, 146.31s, 147.84s, 152.22s.
5	34%; mp 121-122 °C; δ(H): 2.056(3H, s), 2.517(3H, s), 2.650(3H, s), 5.356(2H, s), 5.672(1H s), 6.814 and 6.865(2H, AB-q, J=7.7 Hz), 6.96-7.10(4H, m), 7.34-7.44(4H, m); δ(C): 16.28q, 19.20q, 21.14q, 50.46d, 51.39s, 65.47t, 121.42d, 123.22d, 125.09d, 125.16d, 126.87d, 128.31s, 129.39d, 132.54s, 145.14s, 145.74s, 146.63s, 147.80s, 170.71s.
6	8%; mp 236-237 °C; ms: m/z 330(M^+,80%), 281(100%), 266(92%); δ(H): 2.514(3H, s), 2.826(3H, s), 4.899(2H, s), 5.662(1H, s), 6.807(2H, s), 6.96-7.10(4H, m), 7.30-7.46(4H, m).
7	4%; ms: m/z 354(M^+,41%), 312(100%); δ(H):1.992(3H, s), 2.465(3H, s), 2.667(3H, s), 3.101(2H, s), 5.492(1H, s), 6.773 and 6.864(2H, AB-q, J=7.7 Hz), 7.13-7.37(8H, m).
8	2%; δ(H): 2.407(3H, s), 2.480(3H, s), 2.490(3H, s), 3.302 and 3.523(2H, AB-q, J=16.1 Hz), 5.174(1H, s), 6.863 and 6.925(2H, AB-q, J=7.7 Hz), 6.96-7.04(2H, m), 7.12-7.28(4H, m), 7.32-7.38(2H, m).



Scheme 1.

to form a carbocation. In the usual case, the cation is immediately attacked by a nucleophile in the reaction media or after Wagner-Meerwein rearrangement(s) caused by participation of a neighboring bond.

The present results show that no direct attack of a nucleophile at the α-carbon took place and Wagner-Meerwein rearrangements to homotriptycene skeleton occurred only to a small extent. Instead, the compounds that are thought to be derived from insertion of the α-cation into a C-H bond of the 1-methyl group, **4**, **5**, and **6**, are the major products. We assume for the convenience of discussion that these compounds are formed by way of a pentacoordinated species **10**, or the like, as an intermediate, although we cannot remove the possibility that **10** corresponds to a transition state. If a proton is removed from **10**, the hydrocarbon **4** is formed. **5** and **6** are formed if the hydride shift occurs in **10** to form the stable benzylic cation **11** followed by attack of a nucleophile. It may also be possible to argue that **5** and **6** are formed by direct attack of the nucleophile on **10**, of which the 9-methyl moiety is not attacked by the nucleophile because of steric hindrance.

In discussing the relative amounts of the products from C-H insertion and Wagner-Meerwein rearrangement, we must consider the following points. Firstly, 9-(prim-alkyl)-1,4-dimethyltriptycenes so far studied all exist almost exclusively as ap-rotamer and the rotational barrier about the C_9-C_α bond is about 15 kcal/mol.[10)] These will apply to the present system: the diazonium ion **9**, the direct precursor of the carbocationic species in the reaction, will exist predominantly as ap-rotamer (ap-**9**), and the rotational entity will be retained during the reaction. Secondly, in Wagner-Meerwein rearrangements, the migrating group is always antiperiplanar to the departing species. Thus it is probable that the homotriptycyl cation **12** is formed by participation of the C_9-C_{9a} bond in ap-**9** while **13** by participation of the C_9-C_{8a} bond in ±sc-**9** that is present only in a minute amount; **7** and **8** are produced from **12** and **13**, respectively. It may also be reasonable to assume that participation of the 1-methyl group to form **10** occurs also from the rear of the departing nitrogen, namely in ap-**9**. Therefore, the predominance of the ap-rotamer in the diazonium species as well as the inherent ease of C-H insertion results in the predominant formation of the products via C-H insertion.

Of another interest is the fate of the carbocationic species **10**, that is, the relative ease of proton loss and hydride shift in **10**. Many examples of intramolecular 1,n-hydride shifts, where n is 3 or higher, are known but they usually are not accompanied by proton loss to form cyclized hydrocarbon products.[11] Probably the distance between the relevant carbon atoms is important and the close proximity of the carbons in **10** should favor the ejection of a proton.

In conclusion, we have found that, when a methyl group is placed in a highly congested state with an alkyl cation or its predecessor, the methyl group strongly interact with it to form a pentacoordinated species. This is in accordance with the results of theoretical calculation on the protonated ethane.[12]

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6) Based on the MM2 data of 1,4,9-trimethyltriptycene. We have observed a similar C-H insertion in deamination of ±sc-9-(1-aminomethyl-1-methylethyl)-1,4-dimethyltriptycene, where the distance between the reaction center and the 1-methyl carbon is about 3.2 Å; the details will be reported elsewhere.
7) S. J. Cristol and D. K. Pennelle, J. Org. Chem., 35, 2357 (1979).
8) **2**: mp 213-215 °C; ^{1}H NMR ($CDCl_3$):δ 2.43(3H, s), 2.51(3H, s), ca. 2.8(2H, br s), 4.64(2H, s), 5.59(1H, s), 6.55 and 6.62(2H, AB-q, J=7.8 Hz), 6.8-7.2(4H, m), 7.2-7.8(4H, m).
9) See for example: A. Streitwieser, Jr., J. Org. Chem., 22, 861 (1957); J. H. Ridd, Quart. Rev., 15, 418 (1961); R. H. White and D. J. Woodcock, "The Chemistry of the Amino Group," ed by S. Patai, Interscience (1968), Chap. 8; D. Whittacker, "The Chemistry of Diazonium and Diazo Groups," ed by S. Patai, Interscience (1978), Chap. 14.
10) See for example: M. Ōki, G. Izumi, G. Yamamoto, and N. Nakamura, Bull. Chem. Soc. Jpn., 55, 159 (1982); G. Yamamoto and M. Ōki, ibid., 57, 2219 (1984).
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