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Methyl Group Can Stabilize Carbocations[1)]

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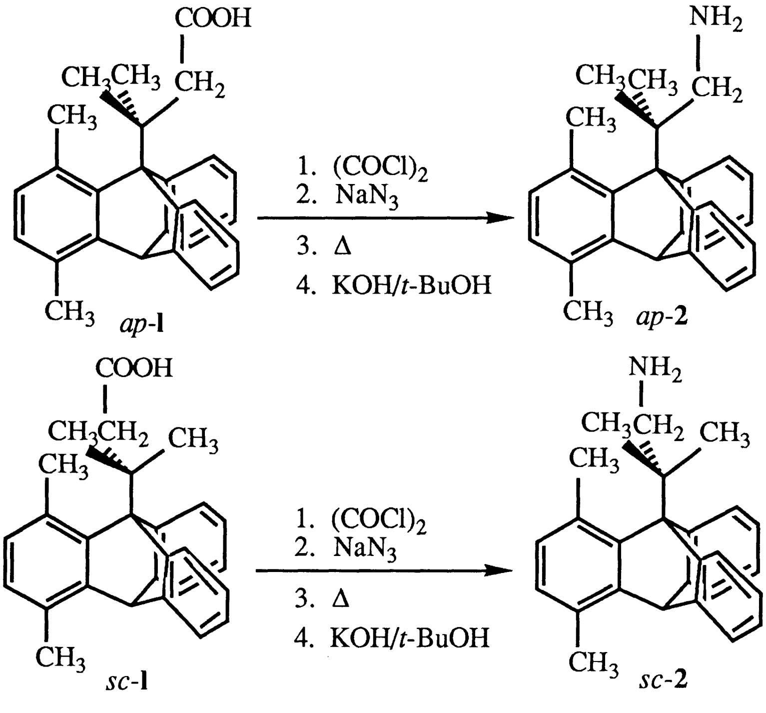
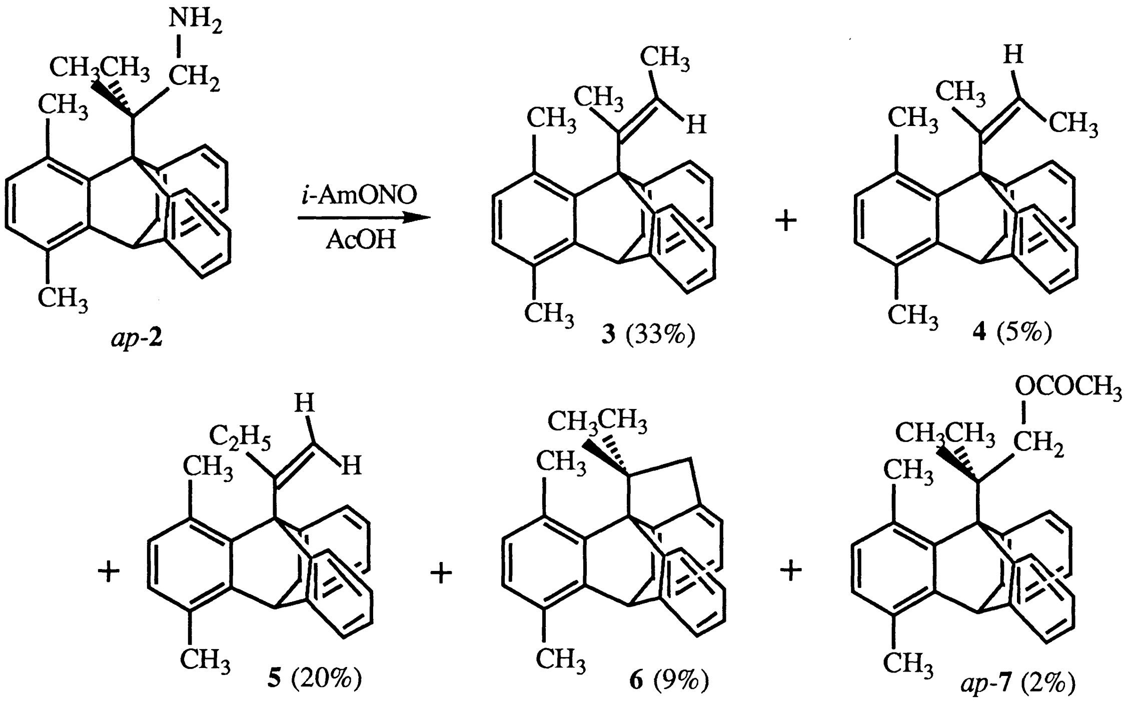
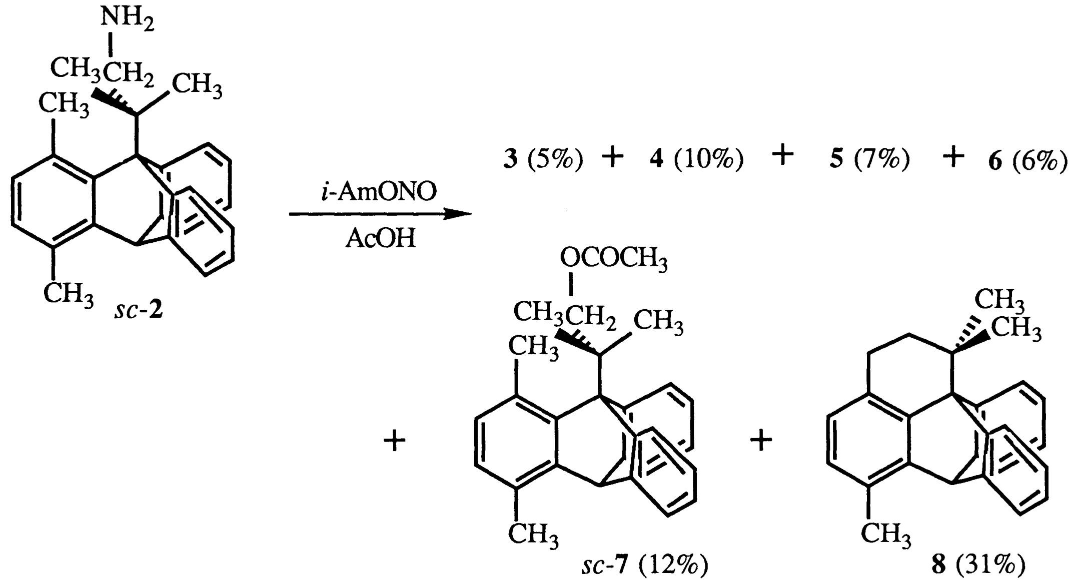
Whereas diazotization of *ap*-2-(1,4-dimethyl-9-triptycyl)-2-methylpropylamine in benzene afforded expected hydrocarbons in addition to a small amount of 2-(1,4-dimethyl-9-triptycyl)-2-methylpropyl acetate, its *sc*-isomer gave 1,1,3-trimethyl-2,3,7,11b-tetrahydro-7,11b-*o*-benzeno-1H-benzo[*de*]anthracene, and a larger amount of the acetate. The results provide unambiguous evidence that the 1-methyl group stabilizes the cation formed by diazotization.

As one of the works on the reactivity of rotational isomers,[2)] we diazotized 2-(1,4-dimethyl-9-triptycyl)-2-methylpropylamine (**2**) and obtained evidence that a methyl group can stabilize carbocations. The preparation of the amine (**2**) from the known[3)] carboxylic acid rotamers (**1**) are shown in the following scheme.



The diazotization of the amines was carried out in the presence of 1 mole of isopentyl nitrite and 2 moles of acetic acid per a mole of the amine in benzene at 80 °C. The products were separated by chromatography and their spectra were compared with the authentic samples[4)] of the possible candidates. The products were the corresponding acetamides in ca. 10% yield and hydrocarbons, together with other minor products. The acetamides derived from the amine and acetic acid together with the acetate (**7**) were easily separated by chromatography. The hydrocarbons were hardly separated by chromatography but compound **8** was isolated in almost a pure





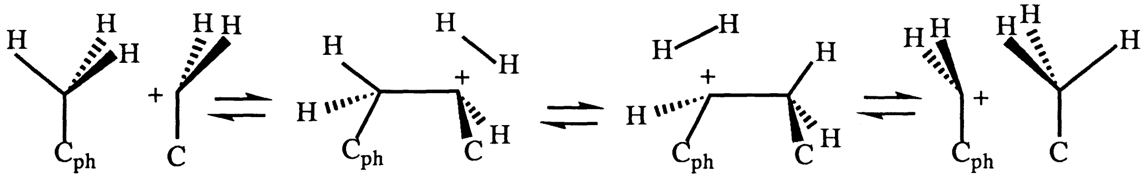
form, thanks to its abundant formation. There was another product in minor quantity from the *ap*-isomer which awaits structural assignment. The yields of these products are given in the scheme with the structures.

The formation of compounds **3**, **4**, **5**, and **6** is common for both rotational isomers. It is interesting to note that the formation of compound **6** takes place, i. e. the cyclization of the produced carbocation takes palce before Wagner-Meerwein rearrangement. This is evidence, at least in this case, that carbocation formation takes place as a discrete step different from that of leaving of nitrogen from the diazonium salt, though such simultaneous rearrangement of the alkyl group with the leaving of nitrogen in the decomposition of diazonium ions is suggested.6) This was pointed out in a previous paper7) by observing absence of products derived from migration of the triptycyl group, which is also the case here.

The yield of the acetate **7** is considerably increased by going from the *ap* form to the *sc*. Participation of the methyl group which is closely located to the cationic center in the case of the *sc* must be considered. The formation of the 6-membered ring compound (**8**) only from the *sc*, irrespective to the fact that both rotamers were treated under the same conditions, also suggests that the 1-methyl group plays a role in the reaction. Both of these imply that a methyl group interacts with a carbocation.

Protonation of hydrocarbons in super acid media was demonstrated as well as carbocation insertion to them by Olah and coworkers.8) $C_2H_7^+$ cation is known in molecular beam study.9) The insertion of carbocations to a C-H bond to form 3-membered rings is known both in nature10) and in laboratory.11) Although these conditions that lead to the insertion of a carbocation into a C-H bond may be thought rather special, the results shown in this paper and that reported earlier from our laboraotry12) as well as others13) indicate that the insertion is rather a common reaction if a carbocation and a hydrocarbon group are located in close proximity.

As an intermediate (transition state) of the reaction, one may postulate a three-membered delocalized cation. However, according to quantum chemical calculations,14,15) the CH_5^+ or $C_2H_7^+$ cations take a structure in which a hydrogen molecule coordinates to an alkyl cation. This structure well explains the formation of the six-membered ring compound (**8**) but not that of the acetate (**7**). As is suggested by Dewar et al.,14) therefore, we have to assume that, in actual reactions, the carbocations react as if they are in the equilibrium as is shown in the following scheme, where both forms, a hydrogen molecule coordinated to a carbocation and a C-H bond coordinated to the cation, are involved. There still remains one problem: why is not 1-acetoxymethyl compound formed if this mechanism operates? A firm answer to this question



cannot be obtained now. We attribute this tentatively to the fact that in benzene a tight ion pair of which freedom is limited prevents the acetate ion to come to proximity of the 1-methyl group.

Summarizing the results, we see that the methyl group has an attractive interaction with carbocations. This anomalous result is a consequence derived by the proximity effects. Although we have neglected such an interaction and have assumed that only the repulsive force operates when a reagent approaches a saturated hydrocarbon group, the results presented in this paper suggest that an attractive force may have to be considered in the transition state of a reaction, where a carbocationic species comes very closely to a saturated hydrocarbon group.

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