Reactivities of Stable Rotamers. XXXV. Diazotization of 2-(1,4-Dimethyl-9-triptycyl)-2-methylpropylamine Rotamers[1,2]

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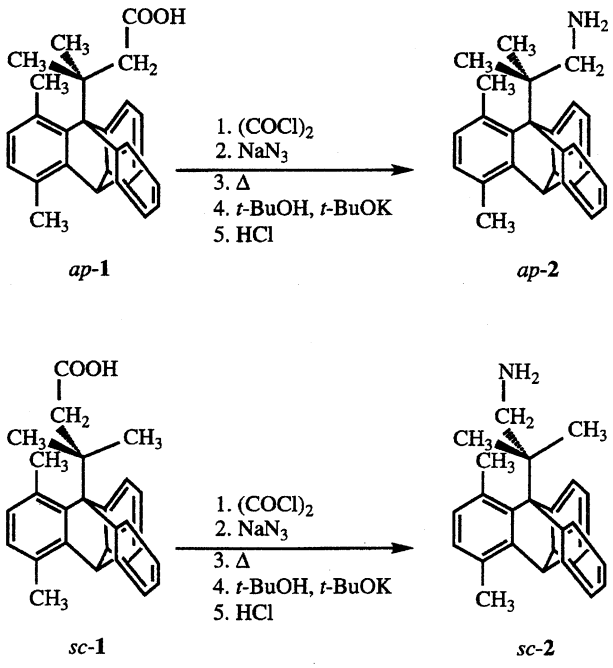
The title amine rotamers were prepared from the corresponding carboxylic acids and were diazotized with isopentyl nitrite in the presence of acetic acid in benzene. The *ap* rotamer affords, as main products, olefins that are derived by deprotonation after rearrangement of the intervening carbocation and small amounts each of the corresponding acetate and a cyclized product, both of which are derived from the unrearranged cation. By contrast, the olefins are minor products and a cyclized product, which is formally derived by insertion of the intervening cation to a C–H bond of the 1-methyl group before rearrangement, is main in the case of the *sc* isomer. This cyclic product was synthesized independently. The yield of the corresponding acetate is increased to a considerable extent in the case of the *sc* relative to the *ap*. These results in the reaction of the *sc* are discussed in terms of stabilization of the intervening cation by the C–H bond.

Differences in reactivities and/or products in reactions of stable rotational isomers in the triptycene series have been reported for 3-(1,4-dimethyl-9-tritptycyl)-3-methylbutanoic acid (**1**)[3,4] and its chloride.[5] The acid function in the rotamers is expected to be transformed to other varieties of functionalities to enable us to examine their reactivities. In this paper, we wish to report, as the first of such papers, the results of diazotization of 2-(1,4-dimethyl-9-triptycyl)-2-methylpropylamine (**2**) rotamers and to discuss the differences observed in these reactions.

The syntheses of amines were carried out by a standard method (Scheme 1). The carboxylic acid (**1**) was converted to the corresponding acid chloride by treating it with oxalyl dichloride and then the chloride was treated with sodium azide. The Curtius rearrangement proceeded smoothly to afford the corresponding isocyanate, when the resulted azide was heated, but the transformation of the isocyanate to the amine posed some difficulties. Finally, the amine (**2**) was obtained in a good yield by treating the isocyanate with potassium *t*-butoxide in *t*-butyl alcohol and then hydrochloric acid.

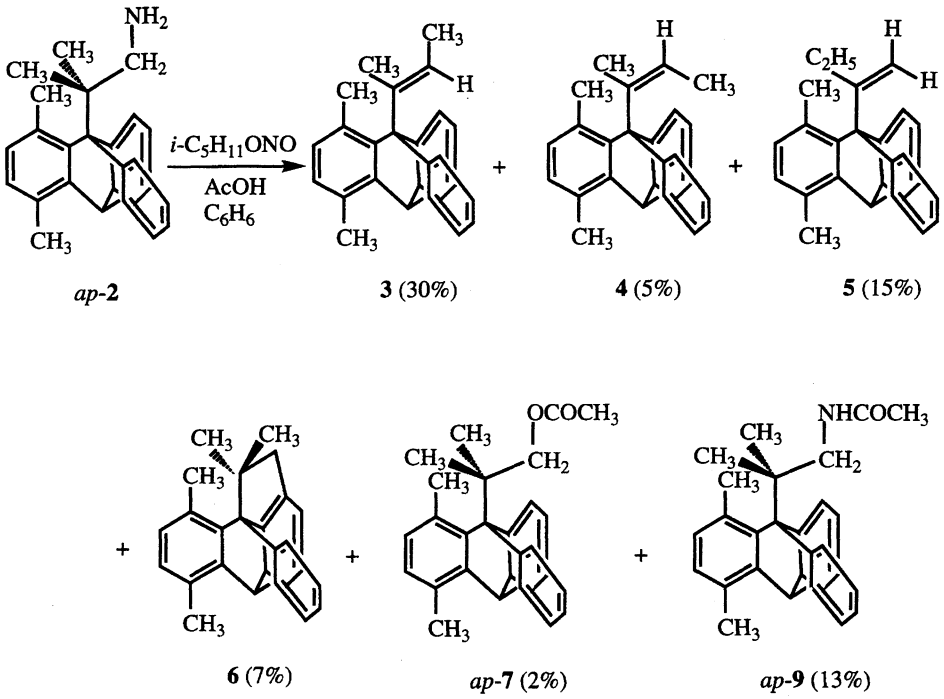


Scheme 1. Syntheses of amine (**2**) rotamers.

Results

The diazotization of the amines (**2**) was carried out with isopentyl nitrite in the presence of acetic acid in boiling benzene. The products were analyzed by ^{1}H NMR by comparing the signal intensities due to the respective compounds of which structures were confirmed by independent synthesis. The synthesis of the cyclized compound (**8**) is described in this paper and those of others are described elsewhere.[6—8]

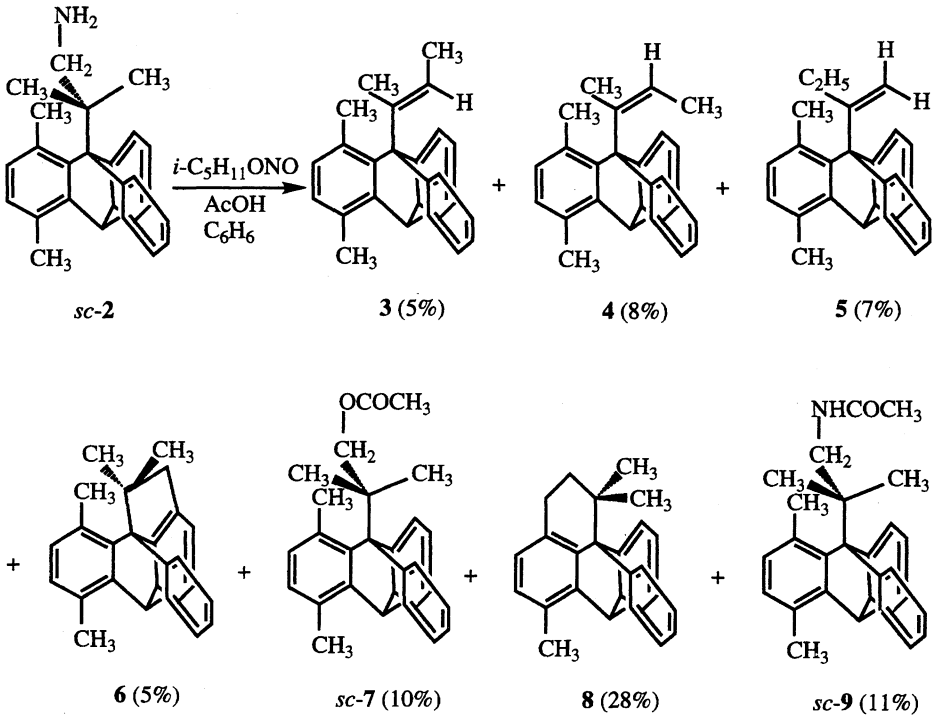
The yields shown in Schemes 2 and 3 are averages of four runs. The acetamides (**9**) derived from **2** were



ap-**2** **3** (30%) **4** (5%) **5** (15%)

6 (7%) *ap*-**7** (2%) *ap*-**9** (13%)

Scheme 2. Results of diazotization of *ap*-**2**.



sc-**2** **3** (5%) **4** (8%) **5** (7%)

6 (5%) *sc*-**7** (10%) **8** (28%) *sc*-**9** (11%)

Scheme 3. Results of diazotization of *sc*-**2**.

inevitably formed to some extent but they are omitted in discussion, because **9**'s are not derived from carbocations. The features of the product distribution are that olefins are main in the case of the *ap*-isomer, whereas the cyclized product **8** is main in the case of the *sc*. It is also noteworthy that the yield of the acetate (*sc*-**7**) is increased considerably in the case of the *sc* with respect to the case of the *ap*.

The solvent effects on the formation ratios were examined. The actual yields of the products together with those in benzene are shown in Tables 1 and 2. Table 3 shows the ratios of the product formations, except the acetamide (**9**), after normalizing to 100%. The reaction was also carried out in ethylene glycol but the material balance was too poor to include the results in the tables. The feature of the data is that the acetate (*sc*-**7**)

Table 1. Effects of Solvents on the Yields (%) of Various Products upon Diazotization of the *ap*-Amine (*ap*-**2**)

Solvent	**3**	**4**	**5**	**6**	*ap*-**7**	*ap*-**9**
Benzene	30	5	15	7	2	13
Acetic acid	35	1	7	10	5	12
Acetonitrile	17	1	4	14	1	38
Ethylene carbonate	23	1	4	6	1	16

Table 2. Effects of Solvents on the Yields (%) of Various Products upon Diazotization of the *sc*-Amine (*sc*-**2**)

Solvent	**3**	**4**	**5**	**6**	*sc*-**7**	**8**	*sc*-**9**
Benzene	5	8	7	5	10	28	11
Acetic acid	2	2	2	2	a)	11	62
Acetonitrile	7	2	5	5	a)	34	17
Ethylene carbonate	5	3	5	4	a)	21	4

a) Not detected.

Table 3. Formation Ratios of Products in Various Solvents on Diazotization of Amines Excluding the Corresponding Acetamide (**9**)

Form	Solvent	**3**	**4**	**5**	**6**	**7**	**8**
ap	C_6H_6	51	8	25	12	3	—
ap	AcOH	60	2	12	17	9	—
ap	MeCN	63	4	15	15	4	—
ap	$C_3H_4O_3$	66	3	11	17	3	—
sc	C_6H_6	8	13	11	8	16	44
sc	AcOH	10	10	10	10	—	58
sc	MeCN	13	4	9	9	—	64
sc	$C_3H_4O_3$	13	8	13	11	—	55

was not detected in any other polar solvents in the case of the *sc* form, whereas acetamide derivatives (**9**) are the main products from the reactions that were carried out in acetic acid. Clearly, solvent affects the fate of the intervening cations but the effects are very small: Although a variety of solvents, of which polarities are different to a large extent, were examined, the change in product distribution is rather small.

One of the points that are noteworthy here is that anything of the product which is expected from the reaction of the intermediates with solvent was not detected. We wish to attribute this result to the steric effects by the substituents imbedded in the substrate.

Synthesis of 1,1,6-Trimethyl-2,3-dihydro-7*H*-7,11b-*o*-benzeno-1*H*-benz[*de*]anthracene (8). Retrosynthesis of this compound indicated that compound **8** could be selectively obtained by starting from 4-methyl-9-anthrone (**10**) for the following reasons. The steps for the synthesis of compound **8** are shown in Scheme 4.

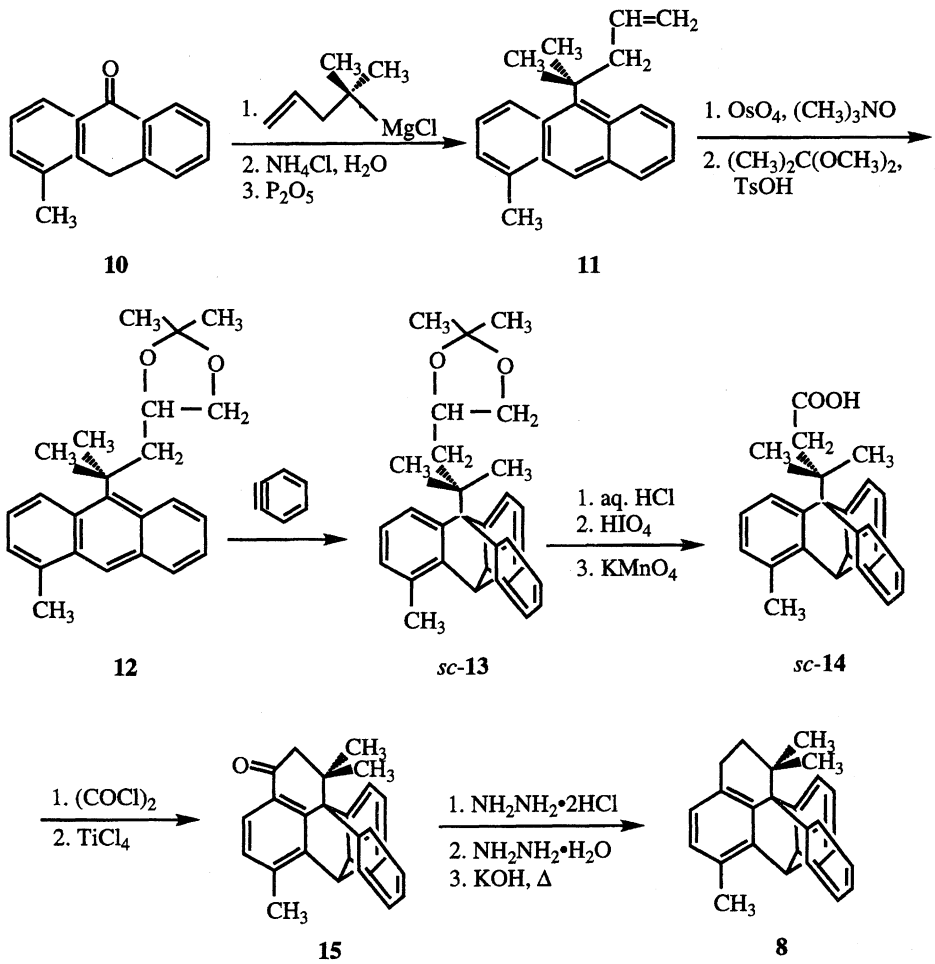
Transformation of compound **10** to 9-(1,1-dimethyl-3-butenyl)anthracene (**11**) is a well known process for us in, for example, the synthesis of compound **1**[3] and a related compound.[9] The anthracene (**11**) could be treated with benzyne to produce the corresponding triptycene but our choice was to convert the olefin part of the compound to an acetonide before converting it to a triptycene because the bulky substituent tends to cause preferential attack from the *ap* direction to it in triptycene syntheses due to the steric effect,[9] the isomer being the one we needed, and it can avoid ene reactions of benzynes. Indeed addition of benzyne to the acetonide (**12**) afforded the desired isomer (*sc*-**13**) with high selectivity and the recrystallization of the product from hexane afforded a pure sample of which stereochemistry was what we needed. Another triptycene stereoisomer (*ap*) was detected by ^{1}H NMR. The formation ratio of the undesired isomer to the desired was ca. 5 : 95. *sc*-**13** was hydrolyzed and the resulted diol was oxidized with periodic acid and then with potassium permanganate to afford a carboxylic acid (*sc*-**14**). Friedel–Crafts cyclization of the acid chloride derived from *sc*-**14** can afford, in principle, two compounds which are formed by cyclization to the peri-position which is para to the existing methyl group and by cyclization to the peri-position of the unsubstituted benzeno bridge. The former reaction must be more facile than the latter because the presence of the methyl group should enhance the reactivity of the benzeno bridge. Indeed, cyclization of the acid chloride in the presence of titanium(IV) chloride at 0 °C afforded the desired ketone (**15**) in ca. 97% and ca. 3% of the undesired isomer. The structures of the isomeric ketones were elucidated by the chemical shift of the methyl-protons attached to the benzene ring. The desired compound gave a signal at δ=1.69, whereas the undesired one at δ=1.43, due to the presence or absence of the carbonyl group para to the methyl. The reduction of the ketone **15** to the hydrocarbon **8** was difficult under normal conditions but was possible under conditions that can be used for hindered ketones.[10]

Although the inferiority of the reaction of **11** with benzyne for the preparation of triptycenes to that of *sc*-**13** were expected, we tried to see how much undesired materials was formed by the reaction. Indeed, there was obtained an unidentified compound, of which spectral and analytical data were very close to a product (**17**) that was derived by isomerization of the ene product, in a fair yield and the yield of the triptycene (*sc*-**16**) was rather low, although the selectivity for the formation of the *sc*-isomer was not so low as expected (Scheme 5).

Discussion

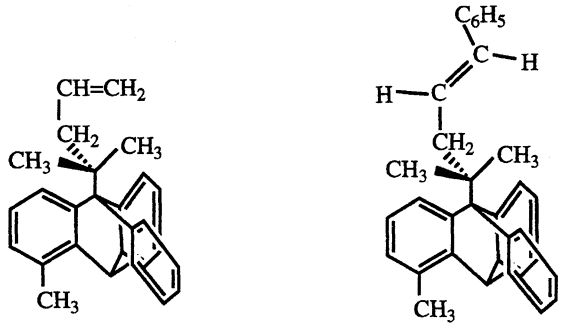
Diazotization of aliphatic primary amines is generally accepted to proceed via diazonium ions in which simultaneous dedinitrogenation and rearrangement of an alkyl group *ap* to the departing nitrogen take place[11] although there is an equilibrium between the diazonium cation and deprotonated diazoalkane, especially in nonpolar solvents.[12—14]

The carbene intermediate (**21**) derived from diazo-



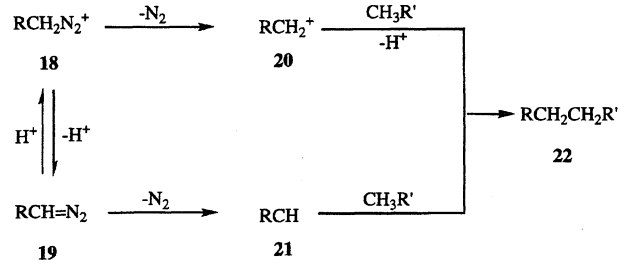
10 **11** **12** ***sc*-13** ***sc*-14** **15** **8**

Scheme 4. Synthetic routes of compound **8**.



***sc*-16** ***sc*-17**

Scheme 5. Products from the reaction of compound **11** with benzyne.



18 **20** **22** **19** **21**

Scheme 6. Possible reaction paths to form the insertion product.

methane **19** which is formed from the diazonium ion (**18**) by deprotonaton is attractive in explaining the formation of **8** (which corresponds to **22** in Scheme 6) because insertion of a carbene to a C–H bond is well-documented.[15] In order to get insight into the reaction, we carried out the same reaction with *sc*-**2**-*N*,*N*-d_2 with acetic acid-d_4 in benzene to see the occurrence of incorporation of deuterium in compound **8**. No deuterium incorporation was observed by ^{2}H NMR spectroscopy. This might be taken as evidence that **8** was exclusively formed via the carbene. However, we prefer the intermediacy of the carbocation for the formation of **8** for the following reasons.

Firstly, the solvent effect speaks against the intermediacy of the carbene. Namely, in the literature, no incorporation of deuterium is reported if diazotization of an amine was carried out in polar solvents and this result is interpreted to indicate that the diazonium cation (**18**) loses nitrogen faster to form the cation (**20**) than loss of proton to form a carbene (**19**) in the polar media. The results in Tables 1, 2, and 3 show that the formation ratios of compound **8** in various solvents are

almost the same. If the mechanisms of the formation of **8** were different from one to another, the formation ratios of **8** to others would be considered to change under different conditions.

Secondly, there are ample examples of the carbocation insertion of the C–H bond in the literature, if a cation is situated closely to the C–H bond. In the biosynthesis of terpenes that contain a cyclopropane ring, the ring is believed to be produced by insertion of a carboncation to a C–H bond.[16] For the synthesis of bicyclo[1.1.0]butane, diazotization of cyclopropylmethylamine is the best method.[17] In the gas phase, $C_2H_7^+$ cation is known.[18] It is also well-known that the C–H insertion of a carbocation takes place in strongly acidic media.[19] It may be argued that this type of reactions takes place under extraordinary conditions, but there are some other examples that show, if a cation is produced in a congested molecule, the cation tends to insert into the C–H bonds.[20—22] Therefore, the carbocation insertion to a C–H bond is a rather general phenomenon.

Thirdly, if the insertion reaction were to proceed via the carbene, we should assume that the carbene formation is very rapid relative to the cation formation and the backward reaction to reform the diazonium salt is very slow to explain the formation of **8** as the major product which is void of deuterium incorporation. However, the literature shows that deuterium incorporation in the diazotization reaction is not so rapid that the backward reactions to form diazonium salts and then carbocations are the main fates of diazoalkanes under the conditions. It may be more appropriate to consider that the diazonium ion was protected from deprotonation by the steric effect, because the CH_2 attached to the positive dinitrogen moiety is located in a congested environment. Thus the diazonium ion exclusively reacts to form the corresponding carbocation.

We thus conclude that formation of **8** occurs via the carbocation insertion to the C–H bond of the 1-methyl group. The next question to be answered is why this kind of insertion was so facile in this compound. We may have to start from discussion about the stability of various cations concerned.

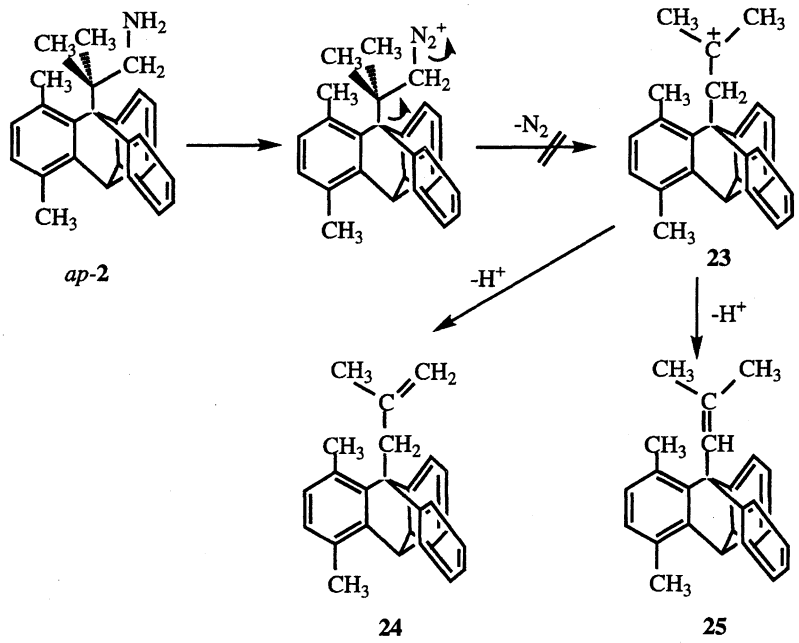
In our triptycene case, the structure is very rigid and the substituent attached to the *t*-butyl group at the 9-position must take an *ap* conformation to the substituent-to-C_9 bond because of the steric effect. This is confirmed by X-ray structure analyses of this type of compounds.[4,23,24] Therefore, if the amines in question were losing nitrogen, after diazotization, with simultaneous migration of an alkyl group, it would be the 9-triptycyl group that migrates (Scheme 7). This migration should have caused formation of 1,1-dimethyl-2-(1, 4-dimethyl-9-triptycyl)ethyl cation (**23**) which would produce olefins **24** and **25** that were prepared independently. However, these olefins were not detected in the products from either of the isomers of **2**.

The reason for the results is that the 9-triptycyl group is reluctant to migrate. This is shown by the results of diazotization of a 9-aminotripycene derivative, which gives stable diazonium ions at −78 °C.[25] This indicates that the 9-triptycyl cation is unusually unstable and dedinitrogenation from the diazonium salt is slow. 9-Bromotriptycene is known not to be hydrolyzed even under very strong conditions[26] because the phenyl group is electron-attracting and, because the cationic center can not assume the planar structure due to the steric constraints. In Wagner–Meerwein rearrangements, a cation-stabilizing group tends to migrate if any of the substituents at the β-position of the departing diazonio group can take the *ap* position.[27] These considerations suggest that the 9-triptycyl group does not migrate simultaneously with the nitrogen departure. Rather a free carbocation (**26**) paired with acetate anion should be formed.

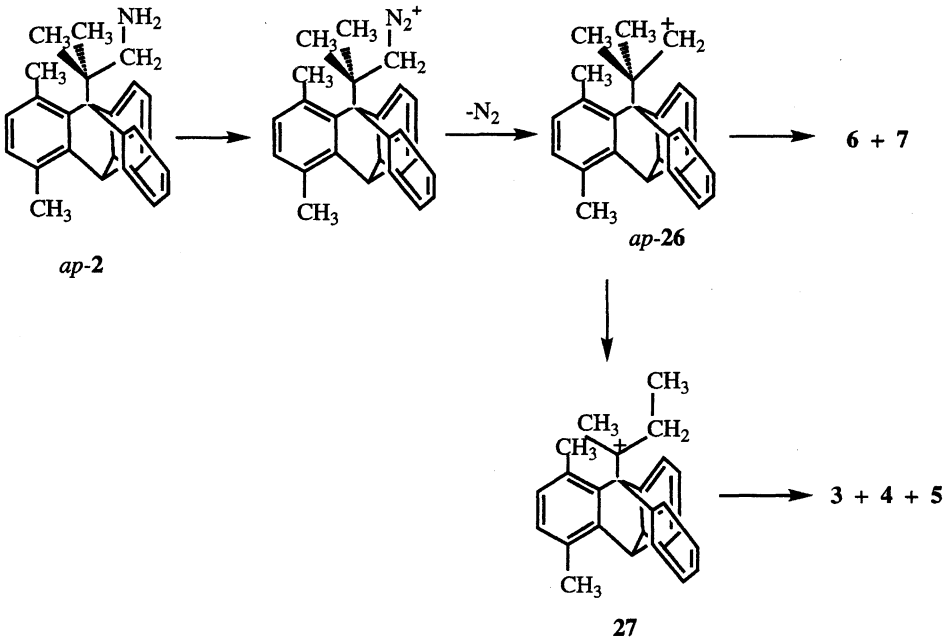
On the basis of the discussion presented above, we can now proceed to the problems of the mechanisms of the reactions and the differences in the products between the rotational isomers. In the case of the *ap* isomer, products derived from the unrearranged carbocation (*ap*-**26**), the 5-membered ring compound and the acetate, were found only in 15% yields in total, and the olefins **3**—**5** are the main products. This is understandable because the cation formed here is primary and should rearrange to the tertiary carbocation (**27**) with ease. We believe the distribution of the olefins is a reflection of kinetic control because the sterically unstable (*Z*)-olefin (**4**) and the 1-ethylvinyl compound (**5**) are produced to a large extent than expected from the thermodynamic distribution.[6,28] The mechanism of the formation of these products may be summarized as in Scheme 8.

The results obtained with the *sc*-isomer are different in several ways from what was observed in the *ap* isomer. The major product is now one that is derived by C–H insertion of the intervening cation (*sc*-**26**) before rearrangement to **27**. The yield of the acetate (*sc*-**7**) also increased considerably. Olefins **3** and **5** decreased in their yields considerably, but the yield of the olefin **4** rather increased from the case of the *ap* of the amine. It is difficult to rationalize the change in the olefin formation from one isomer to another at the moment but it is possible to explain the other differences observed by the participation of the C–H group to the stabilization of the cation. Since the only difference between the *sc* and the *ap* rotamers is the proximity of the 1-methyl group to the cation center (*sc*-**26**), it is natural that we consider the methyl-participation in the reaction (Scheme 9).

It may be argued that the intervening carbocation takes a structure in which the positive charge delocalizes (**28**), like in nonclassical carbocations. However, quantum chemical calculations show that CH_5^+ and other species of penta-coordinated carbon cation



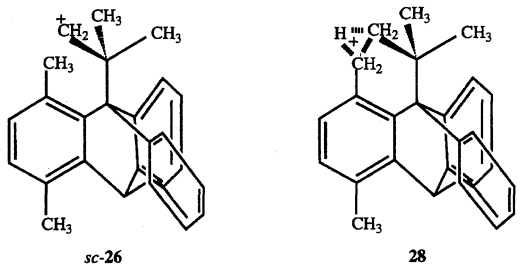
Scheme 7. A possible route of dedinitrogenation and possible products on simultaneous dedinitrogenation and rearrangement.



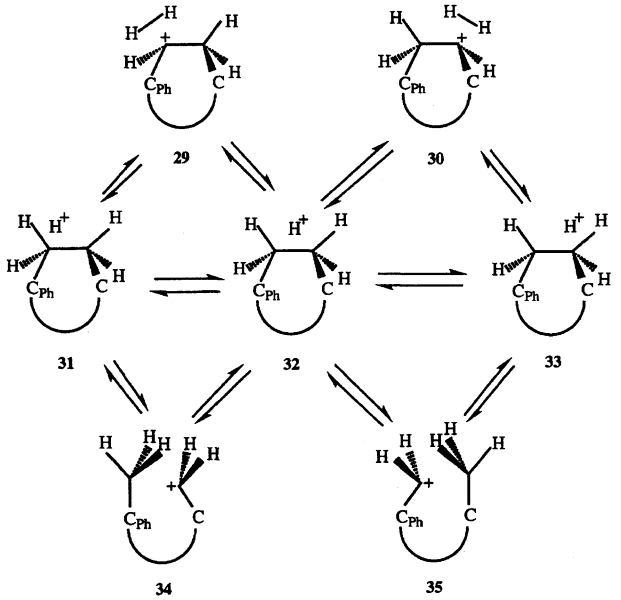
Scheme 8. Possible pathways to the olefins (**3**—**5**) and compounds **6** and **7**.

exist in a form which is approximated by coordination of hydrogen to a carbocation.[29,30] Since the most recent sophisticated calculations also indicate the similar structure,[31—33] we should like to discuss the results with the use of this model (Scheme 10).

If we assume this type of carbocation, then we can describe the cation in question as being in equilibrium among the structures shown in Scheme 10. Here, some of the species, that are exemplified by the C–C coordinated form (**31**—**33**) to proton or the C–H coordinated form (**34** and **35**) to the carbocation, may be unstable relative to those (**29** and **30**), which have the structure of hydrogen-coordinated-to-carbocation, but should exist to some extent at least. If a proton is removed from the form (**31**—**33**) in which the C–C σ-electrons coordinate to a proton, then the formally C–H insertion product is formed. If any of the carbocations (**34** and **35**) stabilized by σ-participation is attacked by the acetate ion present in the system, then the acetate is formed. One of the weak points in this postulate might be that the product formed by attack of the acetate on the 1-carbocation (i. e. from **35**) is absent, though its contribution to the equilibrium must be significant due to the stability of the benzylic cation. We believe this is



Scheme 9. Possible intermediates formed from diazotization of *sc*-**2**.



Scheme 10. Contributing structures of cations in equilibrium.

due to the tightness of the ion pairs in the system. In benzene, ion pairs are so tight that the acetate anion remains at the side chain where it is produced. In addition, the short lifetime of the cation makes the cation to decay before the acetate ion moves from the side chain to the 1-methyl site. Another point of interest is that a product from the proposed intermediates (**29** and **30**), which have the form of hydrogen-coordinated-to-carbocation, is absent in the product. This may mean that these forms are either practically nonexistent or very unreactive. We believe that latter is the case because if the cations **29** and **30** should react with the acetate anion, the attack most likely occurs from the backside of the cation but the approach is blocked because of the structure.

The significant increase in the yield of the acetate (**7**) in the case of *sc*-form does indicate that the participation of the C–H σ-electrons to the stabilization of carbocations is significant. Namely the lifetime of the cation is lengthened to some extent to survive so that it encounters the attack of the acetate ion before rearranging. Although we tend to consider that, if a carbocation approaches an alkyl group, it is only the repulsive force that has to be considered, the present results clearly indicate that, on the contrary to the general belief, these two species exhibit attractive forces when forced to be very close. This conclusion was rather unexpected from the work of comparing the reactivities of rotational isomers but is worthy of note as the general point in organic chemistry.

The solvent affects the yield of the acetate (**7**) seriously. We wish to attribute the absence of **7** in the reactions in solvents other than benzene in the case of *sc* isomer to the polarity of the solvents and to the steric effects. The polar nature of the solvent loosens the ion pairs and the looseness may contribute to lowering the rate of the nucleophilic attack with respect to the rearrangement. The steric effects, which should be more effective in the *sc* form than the *ap*, would more effectively prevent ion-pairing in polar solvents. Although, in ethylene carbonate, the material balance was not good, the formation ratios of compounds were very similar, generally speaking, except the acetamide derivatives (**9**), which were formed much abundantly in acetic acid. The abundant formation of **9** in acetic acid must be attributed to the concentration of acetic acid which wins the competition with the nitrosonium cation in reacting with the amine.

The ratios of the olefins, that were formed after rearrangement, to the products formed before rearrangement of the intervening cation are remarkably constant, grossly speaking. This makes a quite sharp contrast to the general belief that in polar solvents rearrangement is facilitated because of the stabilization of the free cation.[14,34—36] We wish to attribute the results again to the steric effects which more or less level off the solvation effects.

Experimental

^{1}H NMR spectra were measured either on a Varian Gemini 300 or a JEOL GSX-400 spectrometer, operating at 300.1 and 399.8 MHz, respectively, unless otherwise mentioned. Infrared spectra were obtained on a Hitachi I-2000 spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Melting points are not corrected.

***ap*-2-(1,4-Dimethyl-9-triptycyl)-2-methylpropylamine (*ap*-2).** A solution of 200 mg (0.52 mmol) of *ap*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid (*ap*-**1**)[5] in 15 mL of benzene was mixed with 0.60 mL (7.0 mmol) of oxalyl dichloride and stirred for 2 h at room temperature. The solvent and the volatile materials were removed in vacuo at room temperature and the residue was taken up in 10 mL of acetone. To the solution was added an aqueous solution (ca. 0.1 mL) of 34 mg (0.52 mmol) of sodium azide, with ice cooling, and the whole was stirred for 15 min at that temperature. The mixture was poured into water and extracted with benzene. The extract was dried over magnesium sulfate and evaporated after filtration. The residue (azide) exhibited the following spectral absorptions. IR ($CHCl_3$) 1712, 2132 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.39 (6H, s), 2.49 (3H, s), 2.66 (3H, s), 3.65 (2H, s), 5.59 (1H, s), 6.75 (2H, s), 6.97—

7.06 (4H, m), 7.36—7.42 (2H, m), 7.76—7.82 (2H, m).

The acid azide thus obtained was dissolved in 50 mL of benzene and heated under reflux for 2 h. On evaporation of the benzene, the residue (isocyanate) showed the following spectral data. IR ($CHCl_3$) 2268 cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.32 (6H, s), 2.48 (3H, s), 2.64 (3H, s), 4.42 (2H, s), 5.59 (1H, s), 6.75 (2H, s), 6.98—7.04 (4H, m), 7.37—7.39 (2H, m), 7.76 (2H, dd, J=2.5 and 6.5 Hz).

The isocyanate dissolved in 40 mL of tetrahydrofuran was added to a boiling solution of 10 g of potassium hydroxide in 50 mL of *t*-butyl alcohol in 30 min and heated under reflux for 4 h. After cooling, the mixture was diluted with 100 mL of water, acidified with dilute hydrochloric acid up to pH 0, and stirred for 1 h at room temperature. The mixture was basified with potassium hydroxide and extracted with benzene. The extract was washed with aqueous sodium hydrogencarbonate, dried and evaporated after filtration. Hydrogen chloride was passed into a solution of the amine in ether and the amine hydrochloride was collected. *ap*-Amine hydrochloride was obtained in 53% yield. ^1H NMR ($CDCl_3$) δ=2.49 (3H, s), 2.57 (6H, s), 2.63 (3H, s), 4.29 (2H, m), 5.60 (1H, s), 6.76 (2H, s), 6.99—7.05 (4H, m), 7.39 (2H, dd, J=1.4 and 7.2 Hz), 7.91 (2H, d, J=7.5 Hz), 9.11 (3H, br s).

The foregoing amine hydrochloride was mixed with ether and the mixture was shaken with 5% aqueous sodium hydroxide. The free amine was extracted with dichloromethane and the solvent was evaporated after drying over magnesium sulfate. The free *ap*-amine exhibited the following ^1H NMR ($CDCl_3$, δ) data: δ=1.80 (2H, br s), 2.24 (6H, s), 2.48 (3H, s), 2.64 (3H, s), 3.74 (2H, s), 5.58 (1H, s), 6.74 (2H, s), 6.93—7.01 (4H, m), 7.36 (2H, dd, J=2.1 and 6.5 Hz), 7.82 (2H, d, J=7.5 Hz).

The amine was characterized as picrate, mp 243—269 °C (decomp). Found: C, 66.19; H, 5.26; N, 9.59%. Calcd for $C_{32}H_{30}N_4O_7$: C, 65.97; H, 5.19; N, 9.62%.

sc-2-(1,4-Dimethyl-9-tritptycyl)-2-methylpropylamine (*sc*-2). This compound was prepared similarly as *ap*-**2** from the corresponding carboxylic acid.[5] The following spectral data were recorded for the intermediates.

Acid Azide: ^1H NMR ($CDCl_3$) δ=2.26 (3H, s), 2.32 (3H, s), 2.52 (3H, s), 2.68 (3H, s), 3.71 and 3.89 (2H, ABq, J=16.8 Hz), 5.59 (1H, s), 6.77 and 6.79 (2H, ABq, J=7.9 Hz), 6.97—7.03 (4H, m), 7.34—7.38 (2H, m), 7.71—7.74 (1H, m), 7.80—7.82 (1H, m); IR ($CHCl_3$) 1712 and 2136 cm^{-1}.

Isocyanate: ^1H NMR ($CDCl_3$) δ=2.14 (3H, s), 2.17 (3H, s), 2.52 (3H, s), 2.57 (3H, s), 4.32 and 4.82 (2H, ABq, J=14.2 Hz), 5.59 (1H, s), 6.77 and 6.79 (2H, ABq, J=7.9 Hz), 6.93—7.03 (4H, m), 7.31—7.40 (2H, m), 7.73 (1H, dd, J=2.2 and 6.7 Hz), 7.84 (1H, m); IR ($CHCl_3$) 2272 cm^{-1}.

The hydrochloride of *sc*-**2** was obtained in 59% total yield from the corresponding carboxylic acid. ^1H NMR ($CDCl_3$) δ=2.30 (3H, s), 2.33 (3H, s), 2.41 (3H, s), 2.76 (3H, s), 4.31 (1H, m), 4.59 (1H, m), 5.60 (1H, s), 6.72—6.80 (2H, m), 6.97—7.10 (4H, m), 7.35—7.42 (2H, m), 7.81 (1H, br m), 7.91 (1H, d, J=8.1 Hz), 9.13 (3H, br m).

The *sc*-amine showed the following ^1H NMR spectra ($CDCl_3$, δ): δ=1.88 (2H, br), 2.05 (3H, s), 2.07 (3H, s), 2.50 (3H, s), 2.60 (3H, s), 3.64 and 4.06 (2H, ABq, J=14.9 Hz), 5.58 (1H, s), 6.75 and 6.77 (2H, ABq, J=8.0 Hz), 6.92—7.02 (4H, m), 7.32—7.38 (2H, m), 7.86—7.92 (2H, m).

The amine was characterized as picrate, mp 201—203 °C. Found: C, 65.65; H, 5.12; N, 9.37%. Calcd for $C_{32}H_{30}N_4O_7$: C, 65.97; H, 5.19; N, 9.62%.

Diazotization of Amine. The *ap*-amine (44.4 mg or 0.126 mmol) was dissolved in 7.5 mL of benzene and the solution was heated under reflux with 17.0 μL (0.126 mmol) of isopentyl nitrite and 13.6 μL (0.250 mmol) of acetic acid for 1 h under an argon atmosphere. After cooling, the mixture was diluted with dichloromethane, and the solution was washed with water and dried. After evaporation of the solvent, the product was separated by preparative TLC (Merck, silica gel 60 F_{254}, 2 mm) with 1:2 dichloromethane–hexane, which gave three fractions. The first fraction contained olefins and the 5-membered ring compound, the second fraction the acetate, and the third fraction the acetamide. The formation ratios of these products were obtained by referring to the NMR spectra[6—8] of the products before fractionating. The yield of the acetamide was 13%.

The *sc*-amine was similarly treated and the products were analyzed similarly. In this case, the 6-membered ring compound was contained in the first fraction with other hydrocarbons to make the composition of the mixture more complex than the case of the *ap*-amine. The acetamide was obtained in 11% yield.

***N*-[2-(1,4-Dimethyl-9-triptycyl)-2-methylpropyl]-acetamide (9).** This was prepared by treating the free amine with acetic anhydride.

The *ap*-amide recrystallized from THF–hexane, mp 240.5—242.5 °C. Found: C, 84.78; H, 7.30; N, 3.79%. Calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.54%. ^1H NMR ($CDCl_3$) δ=2.15 (3H, s), 2.23 (6H, s), 2.48 (3H, s), 2.61 (3H, s), 4.45 (2H, d, J=6.5 Hz), 5.58 (1H, s), 6.09 (1H, br m), 6.73 (2H, s), 6.97—7.03 (4H, m), 7.35—7.37 (2H, m), 7.99 (2H, m).

The *sc*-amide recrystallized from THF–hexane, mp 256—257 °C. Found: C, 84.79; H, 7.19; N, 3.34%. Calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.54%. ^1H NMR ($CDCl_3$) δ=2.08 (3H, s), 2.12 (3H, s), 2.17 (3H, s), 2.52 (3H, s), 2.63 (3H, s), 4.08 (1H, dd, J=15.0 and 5.1 Hz), 5.00 (1H, dd, J=15.0 and 7.5 Hz), 5.59 (1H, s), 5.90 (1H, br m), 6.74 and 6.80 (2H, ABq, J=7.9 Hz), 6.97—7.03 (4H, m), 7.34—7.38 (2H, m), 7.81 (1H, m), 8.06 (1H, dd, J=1.8 and 7.0 Hz).

1-Methylanthraquinone. To a solution of 25.0 g (0.158 mol) of 1,4-naphthoquinone and 47.3 mL (0.474 mol) of 1,3-pentadiene in 150 mL of dichloromethane was slowly added 38.9 mL (0.316 mol) of trifluoroborane-ether complex at 0 °C and the mixture was stirred for 2 h at room temperature. The mixture was washed with water and the dichloromethane solution was dried. After evaporation of the solvent, the residue was treated with methanol to afford the desired compound in 23% yield, mp 171.5—172.5 °C (lit, mp 171—172 °C).[37,38] ^1H NMR ($CDCl_3$) δ=2.87 (3H, s), 7.59 (1H, d, J=7.9 Hz), 7.65 (1H, t, J=7.5 Hz), 7.74—7.82 (2H, m), 8.25—8.29 (3H, m).

4-Methyl-9-anthrone (10). A mixture of the foregoing anthraquinone (10.3 g or 46.5 mmol) and 28.6 g (163 mmol) of sodium dithionite in 350 mL of 1 mol L^{-1} aqueous sodium hydroxide was heated under reflux for 3 h and the crystals obtained upon cooling were collected by filtration. The crystals were purified by chromatography over silica gel (1:1 hexane–dichloromethane eluent) and then recrystallized from hexane–dichloromethane to give 43% of the desired compound, mp 127.5—130.0 °C (lit, mp 127—129.5

°C).[39] ^{1}H NMR ($CDCl_3$) δ=2.42 (3H, s), 4.11 (2H, s), 7.36 (1H, t, J=7.7 Hz), 7.43—7.50 (3H, m), 7.58 (1H, dt, J=1.3 and 7.4 Hz), 8.25 (1H, d, J=7.5 Hz), 8.34 (1H, dd, J=8.0 and 1.9 Hz).

The isomer of **10**, 1-methyl-9-anthrone, was obtained in 15% yield in the same treatment, mp 90—91 °C.[40] ^{1}H NMR ($CDCl_3$) δ=2.84 (3H, s), 4.30 (2H, s), 7.20 (1H, d, J=7.2 Hz), 7.29 (1H, d, J=7.3 Hz), 7.38—7.44 (3H, m), 7.53 (1H, dt, J=7.5 and 1.4 Hz), 8.24 (1H, dd, J=7.7 and 1.2 Hz).

9-(1,1-Dimethyl-3-butenyl)-4-methyl-9-anthrol. A Grignard reagent was prepared from 2.95 g (121 mmol) of magnesium and 7.20 g (60.7 mmol) of 4-chloro-4-methyl-1-pentene[41] in tetrahydrofuran with the aid of 11.7 g (60.7 mmol) of 1,2-dibromoethane. The tetrahydrofuran used for the preparation was 93 mL in total. The mixture was cooled with ice and 4-methyl-9-anthrone (3.62 g or 30.3 mmol) was added in portions. The mixture was stirred for 1 h after addition of the anthrone at room temperature and was heated under reflux for 1 h. The mixture was decomposed with aqueous ammonium chloride and the organic materials were extracted with benzene. The extracts were dried over magnesium sulfate and the solvent was evaporated after filtration. The residue was purified by chromatography on silca gel with hexane as eluent. An almost pure sample was obtained in 69% yield. ^{1}H NMR ($CDCl_3$) δ=0.76 (3H, s), 0.80 (3H, s), 2.05 (2H, d, J=6.9 Hz), 2.44 (3H, s), 2.63 (1H, s), 3.87 and 3.93 (2H, ABq, J=16.0 Hz), 4.88 (1H, dd, J=2.3 and 10.0 Hz), 4.94 (1H, dd, J=2.3 and 16.6 Hz), 5.68—5.77 (1H, m), 7.18 (1H, d, J=7.2 Hz), 7.20—7.33 (4H, m), 7.80 (1H, d, J=7.6 Hz), 7.86 (1H, d, J=7.6 Hz). This compound was directly used for the next synthesis.

10-(1,1-Dimethyl-3-butenyl)-1-methylanthracene (11). A solution of 1.76 g (60.2 mmol) of the anthrol in 75 mL of carbon tetrachloride was heated under reflux with 19.0 g (134 mmol) of phosphorus pentaoxide for 30 min. The solid material was removed by filtration and the solvent was evaporated. The residue was submitted to chromatography on silica gel (hexane eluent) and the compound was obtained as an oil of ca. 90% purity. ^{1}H NMR ($CDCl_3$) δ=1.82 (6H, s), 2.78 (3H, s), 3.15 (2H, d, J=7.2 Hz), 4.92 (1H, dd, J=1.0 and 9.6 Hz), 5.03 (1H, dd, J=1.0 and 17.0 Hz), 5.62 (1H, m), 7.13—7.21 (2H, m), 7.26—7.38 (2H, m), 7.97 (1H, dd, J=1.8 and 8.1 Hz), 8.36 (1H, m), 8.39 (1H, s), 8.49 (1H, d, J=8.8 Hz).

***sc*-10-(1,1-Dimethyl-3-butenyl)-1-methyltriptycene (*sc*-16).** The anthracene (4.47 g, 16.3 mmol) and 2.2 mL (16 mmol) of isopentyl nitrite were dissolved in 300 mL of dichloromethane. The solution was heated under reflux and, to this solution were simultaneously added a solution of 4.47 g (32.6 mmol) of anthranilic acid in 90 mL of acetone and another of 4.8 mL (36 mmol) of isopentyl nitrite in 90 mL of dichloromethane from separate separatory funnels. The mixture was heated under reflux for 2 h after addition of the solutions and the solvent was evaporated. The residue was submitted to chromatography on silica gel (hexane eluent) to afford the desired compound in 64% yield and another unidentified compound. The desired compound was recrystallized from methanol-dichloromethane and melted at 144—145 °C. Found: C, 92.74; H, 7.59%. Calcd for $C_{27}H_{26}$: C, 92.52; H, 7.48%. ^{1}H NMR ($CDCl_3$) δ=2.06 (3H, s), 2.07 (3H, s), 2.53 (3H, s), 3.33 (2H, d, J=7.7 Hz), 5.23—5.51 (2H, m), 5.54 (1H, s), 6.21—6.35 (1H, m), 6.82—6.89 (2H, m), 6.93—7.01 (4H, m), 7.34—7.40 (2H, m), 7.63 (1H, dd, J=2.6 and 6.5 Hz), 7.72—7.80 (2H, m).

The unidentified compound (most probably *sc*-**17**) was purified by recrystallization from hexane, mp 178—180 °C. It was obtained in 16% yield. Found: C, 93.00; H, 7.25%. Calcd for $C_{33}H_{30}$: C, 92.91; H, 7.09%. ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.22 (3H, s), 2.52 (3H, s), 3.44 (2H, d, J=7.2 Hz), 5.58 (1H, s), 6.05 (1H, dt, J=15.8 and 7.2 Hz), 6.81—7.05 (7H, m), 7.18—7.27 (3H, m), 7.30—7.43 (4H, m), 7.56 (1H, m), 7.69 (1H, d, J=7.3 Hz), 7.79 (1H, m). These NMR data clearly indicate that the compound is not a simple ene product, because if it were a case, two olefinic proton signals should appear at δ=5—6. We believe that isomerization of the ene product to *sc*-**17** took place by the influence of acid(s). In *sc*-**17**, it is possible that one of the olefinic protons gives its signal in the aromatic region. The coupling constant of the signal at δ=6.05 clearly indicates that the olefin is most likely trans.

4-Methyl-4-(4-methyl-9-anthryl)pentane-1,2-diol. A solution of 1.10 g (4.01 mmol) of the foregoing anthracene (**11**) in 55.0 mL of *t*-butyl alcohol was mixed with 0.89 g (7.99 mmol) of trimethylamine oxide dihydrate, 2.2 mL of pyridine, 15.0 mL of water, and 18.0 mg of osmium tetraoxide and the whole was heated under reflux for 17 h under an argon atmosphere. The mixture was cooled, washed with 20% aqueous sodium hydrogensulfite, and extracted with dichloromethane. The diol exhibited the following ^{1}H NMR spectra ($CDCl_3$): δ=1.83 (3H, s), 1.91 (3H, s), 2.44—2.60 (2H, m), 2.75 (2H, br), 2.78 (3H, s), 3.21—3.36 (2H, m), 3.78 (1H, m), 7.16—7.43 (4H, m), 7.97 (1H, dd, J=2.3 and 7.6 Hz), 8.39—8.57 (3H, m).

2,2-Dimethyl-4-[2-(4-methyl-9-anthryl)-1,1-dimethylethyl]-1,3-dioxolane (12). A solution of 0.93 g (3.0 mmol) of the above diol in 25 mL of benzene was mixed with 57 mg of *p*-toluenesulfonic acid monohydrate and 1.90 mL (15.5 mmol) of acetone dimethyl acetal and the whole was stirred for 10 h at room temperature. The mixture was washed with 5% aqueous sodium hydrogencarbonate and the aqueous washings were extracted with dichloromethane. The organic layers were combined and dried over magnesium sulfate. The solvent was evaporated after filtration and the residue was submitted to silica-gel chromatography (4:1 hexane–dichloromethane eluent) to afford the desired compound in almost a pure state in 56% yield. ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, s), 1.39 (3H, s), 1.83 (3H, s), 1.93 (3H, s), 2.50 (1H, dd, J=14.7 and 6.6 Hz), 2.79 (3H, s), 2.92 (1H, dd, J=14.7 and 4.8 Hz), 3.22 (1H, t, J=8.1 Hz), 3.50 (1H, dd, J=8.1 and 5.7 Hz), 4.11 (1H, m), 7.18—7.23 (2H, m), 7.29—7.40 (2H, m), 7.98 (1H, dd, J=2.0 and 7.8 Hz), 8.40 (1H, m), 8.42 (1H, s), 8.53 (1H, d, J=8.5 Hz).

***sc*-9-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)-1,1-dimethylethyl]-4-methyltriptycene (13).** To a boiling solution of 377 mg (1.08 mmol) of the anthracene (**12**) and 145 μL (1.08 mmol) of isopentyl nitrite in 25 mL of dichloromethane were added simultaneously from two syringes a solution of 296 mg (2.16 mmol) of anthranilic acid in 5 mL of acetone and a solution of 319 μL (2.37 mmol) of isopentyl nitrite in 5 mL of dichloromethane in 5 h. The mixture was further heated under reflux for 1 h after the addition was over. The solvents were evaporated and the residue was submitted to chromatography on silica gel (4:1 hexane–dichloromethane eluent) to give the desired material

in 83% yield. The material was further purified by recrystallization from dichloromethane–hexane, mp 192.5—195.0 °C. ^{1}H NMR indicated that it was apparently a mixture of two diastereomers. The following signals for the major isomer were detected in the aliphatic region ($CDCl_3$): δ=1.48 (3H, s), 1.50 (3H, s), 2.10 (3H, s), 2.19 (3H, s), 2.51 (3H, s), 2.64—2.72 (1H, m), 2.85—2.96 (1H, m), 3.55—3.62 (1H, m), 4.18—4.25 (1H, m), 4.67—4.76 (1H, m), 5.53 (1H, s).

***sc*-3-Methyl-3-(4-methyl-9-triptycyl)butanal.** A solution of 192 mg of the compound **13** in 5.0 mL of tetrahydrofuran was stirred with 5.0 mL of 1 mol L^{-1} hydrochloric acid for 16 h at room temperature and poured into water. The mixture was extracted with dichloromethane. The extract was dried over magnesium sulfate and the solvent was evaporated after filtration. The product was submitted to silica-gel chromatography (dichloromethane eluent) to afford 98% of the corresponding diol.

A solution of 171 mg (0.44 mmol) of the diol in 4.0 mL of tetrahydrofuran was mixed with 254 mg (1.11 mmol) of periodic acid dihydrate and 1.0 mL of water and stirred for 4 h at room temperature. The mixture was diluted with water and extracted with dichloromethane. The extracts were dried over magnesium sulfate and the solvent was evaporated after filtration. The residue was submitted to silica-gel chromatography (dichloromethane eluent) to afford the desired compound in 85% yield. The compound was further purified by recrystallization from dichloromethane–hexane, mp 202.5—205.5 °C. Found: C, 88.28%; H, 6.92%. Calcd for $C_{26}H_{24}O$: C, 88.60; H, 6.86%. ^{1}H NMR ($CDCl_3$) δ=2.28 (3H, s), 2.29 (3H, s), 2.53 (3H, s), 3.71 (2H, br s), 5.54 (1H, s), 6.82—6.91 (2H, m), 6.96—7.04 (4H, m), 7.37—7.43 (2H, m), 7.57 (1H, d, J=7.7 Hz), 7.68—7.73 (2H, m), 10.26 (1H, t, J=2.7 Hz).

This aldehyde was obtained similarly starting from the butenyltriptycene (*sc*-**16**), via a diol formation and oxidation, in ca. 60% yield.

***sc*-2-Methyl-2-(4-methyl-9-triptycyl)butanoic Acid (*sc*-14).** To a solution of 133 mg (0.377 mmol) of the aldehyde in 4.5 mL of acetone, was added 65.5 mg (0.414 mmol) of potassium permanganate and 65.5 mg (0.065 mmol) of sodium hydrogencarbonate with ice-cooling, and the mixture was stirred at room temperature for 1 h. Aqueous sodium hydrogensulfite was added to destroy the excess of the permanganate and the whole was stirred for 1 h. The mixture was extracted with dichloromethane and the solvent was evaporated. The carboxylic acid was purified by recrystallization from hexane–dichloromethane, mp 237.0—239.5 °C. It was obtained in 68% yield. ^{1}H NMR ($CDCl_3$) δ=2.27 (3H, s), 2.28 (3H, s), 2.54 (3H, s), 3.64 (2H, s), 5.56 (1H, s), 6.86—6.93 (2H, m), 6.98—7.05 (4H, m), 7.37—7.42 (2H, m), 7.68 (1H, d, J=7.7 Hz), 7.75—7.77 (1H, m), 7.82—7.84 (1H, m), ca. 11.1 (1H, very br s).

1,1,6-Trimethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benzo[*de*]anthracen-3-one (15). A solution of 137 mg (0.372 mmol) of the carboxylic acid in 10 mL of benzene and 450 μL (5.13 mmol) of oxalyl dichloride were stirred at room temperature for 2 h and the volatile materials were evaporated. The residue taken up in 15.0 mL of dichloromethane was treated with 82.0 μL (0.748 mmol) of titanium(IV) chloride and the whole was stirred for 2 h with ice-cooling. The mixture was treated with water and extracted with dichloromethane. The extract was dried and the solvent evaporated. The residue was submitted to chromatography on silica gel (dichloromethane eluent) to give the desired compound in 88% yield. The analytical sample was obtained by recrystallization from tetrahydrofuran–hexane, mp 256—257 °C. Found: C, 89.33; H, 6.09%. Calcd for $C_{26}H_{22}O$; C, 89.11; H, 6.33%. ^{1}H NMR ($CDCl_3$) δ=1.69 (3H, d, J=1.0 Hz), 2.14 (3H, s), 2.56 (3H, s), 2.67 and 3.48 (2H, ABq, J=14.7 Hz), 5.56 (1H, s), 6.91—7.00 (3H, m), 7.05—7.13 (2H, m), 7.32 (1H, dd, J=1.5 and 7.0 Hz), 7.50 (1H, dd, J=1.7 and 6.8 Hz), 7.53 (1H, d, J=7.9 Hz), 7.77 (1H, d, J=7.5 Hz), 7.85 (1H, J=7.9 Hz); IR ($CHCl_3$) 1684 cm^{-1}.

1,1,6-Trimethyl-2,3-dihydro-7*H*-7,11b-*o*-benzeno-1*H*-benzo[*de*]anthracene (8). A solution of 100 mg (0.285 mmol) of the ketone, 240 mg (2.29 mmol) of hydrazine dihydrochloride, and 0.30 mL (6.2 mmol) of hydrazine hydrate in 30 mL of triethylene glycol was heated under reflux at 130 °C for 2.5 h. To the cooled mixture was added 350 mg (6.24 mmol) of potassium hydroxide and the mixture was heated to allow volatile materials to distill out until the inside temperature became 210 °C. The mixture was heated under reflux at that temperature for 2 h and cooled. Water was added to the mixture and organic materials were extracted with dichloromethane. After the usual treatment the product was chromatographed on silica gel (dichloromethane eluent) and recrystallized from dichloromethane–hexane, mp 201—202 °C. The yield was 98%. Found: C, 92.62; H, 7.35%. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%. ^{1}H NMR ($CDCl_3$) δ=1.60 (3H, s), 1.76—1.81 (1H, m), 2.07 (3H, s), 2.48 (3H, s), 2.50—2.61 (2H, m), 3.14—3.21 (1H, m), 5.47 (1H, s), 6.68 and 6.76 (2H, ABq, J=7.7 Hz), 6.80—6.91 (2H, m), 6.99—7.06 (2H, m), 7.22 (1H, dd, J=1.4 and 7.2 Hz), 7.42 (1H, dd, J=1.9 and 7.0 Hz), 7.68 (1H, d, J=7.2 Hz), 7.87 (1H, dd, J=1.7 and 8.0 Hz).

9-(2-Methyl-2-propenyl)-9-anthrol. A Grignard reagent was prepared from 2.6 g (0.11 mol) of Mg in 6.6 mL THF and 4.84 g (53.4 mmol) of 3-chloro-2-methyl-1-propene and 4.6 mL (53 mmol) of 1,2-dibromoethane in 35 mL of THF. The solution was diluted with 4 mL of THF and, to the solution, was added 3.24 g (16.7 mmol) of anthrone in portions. The mixture was stirred for 1 h at room temperature and then refluxed for another hour. The mixture was decomposed with saturated aqueous ammonium chloride and the aqueous layer was extracted with ether. After evaporation of the solvent, the residue was treated with hexane to remove insoluble anthrone. The filtrate was evaporated and the residue was purified by chromatography on silica gel (hexane eluent). The yield was 63%. It was used directly for the next reaction.

9-(2-Methyl-2-propenyl)anthracene. The anthrol (0.50 g or 2.0 mmol) in 30 mL of benzene was mixed with 2.3 mL of pyridine and 1.20 mL (17.0 mmol) of thionyl chloride and the mixture was heated under reflux, the completion of the reaction being checked by TLC. It was ca. 30 min. After cooling, water was added to decompose excess of thionyl chloride and the aqueous layer was extracted with benzene. After evaporation of the solvent, the residue was submitted to alumina chromatography (hexane eluent). The desired compound was obtained in 93% yield. Mp 61—62 °C. It was recrystallized from hexane. Found: C, 92.95; H, 6.75%. Cacld for $C_{18}H_{16}$: C, 93.06; H, 6.94%. ^{1}H NMR ($CDCl_3$) δ=1.97 (3H, s), 4.24 (1H, m), 4.28 (2H, s), 4.79 (1H, m),

7.42—7.52 (4H, m), 8.01 (2H, dd, J=7.5 and 2.1 Hz), 8.16 (2H, d, J=8.3 Hz), 8.38 (1H, s).

1,4-Dimethyl-9-(2-methyl-2-propenyl)triptycene (24). This triptycene was prepared similarly as above using the anthracene in dichloromethane, 3,6-dimethylanthranilic acid[42] in acetone and isopentyl nitrite in dichloromethane. It was purified by chromatography (hexane eluent) and recrystallization from methanol, mp 145—147 °C. Yield 49%. Found: C, 92.76; H, 7.43%. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%. ^{1}H NMR ($CDCl_3$, r.t.) δ=2.12 (3H, s), 2.2—2.8 (6H, br), 3.2—4.7 (3H, br), 4.98 (1H, br s), 5.60 (1H, s), 6.4—6.8 (2H, br), 6.8—7.1 (4H, br m), 7.1—7.5 (4H, br m). This compound showed the presence of two rotational isomers at −30 °C. ^{1}H NMR ($CDCl_3$, −30 °C) δ=2.14 (*ap*-3H, *sc*-3H, s), 2.44 (*ap*-3H, s), 2.49 (*sc*-3H, s), 2.53 (*sc*-3H, s), 2.65 (*ap*-3H, s), 3.41 and 3.86 (*sc*-2H, ABq, J=18.8 Hz), 3.94 (*ap*-3H, br s), 4.49 (*sc*-1H, s), 4.97 (*ap*-1H, s), 5.01 (*sc*-1H, s), 5.64 (*sc*-1H, s), 5.65 (*ap*-1H, s), 6.55 (*ap*-1H, d, J=7.5 Hz), 6.63 (*ap*-1H, *sc*-1H, m), 6.76 (*sc*-1H, d, J=7.5 Hz), 6.88—7.06 (*ap*-4H, *sc*-4H, m), 7.29—7.44 (*ap*-4H, *sc*-4H, m). The population ratio of *ap* and *sc* isomers was 1.00:0.79 at this temperature.

9-(2-Methyl-1-propenyl)anthracene. A Grignard reagent was prepared similarly from 1-bromo-2-methyl-1-propene in THF. Anthrone was added and addition product was obtained. This anthrol spontaneously lost water on subsequent treatment, and the anthracene was obtained. It was purified by chromatography on silica gel (hexane eluent) and recrystallization from hexane, mp 57—59 °C. Yield was 63%. Found; C, 93.14; H, 6.91%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%. ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, s), 2.17 (3H, d, J=1.5 Hz), 6.78 (1H, m), 7.41—7.48 (4H, m), 8.00 (2H, m), 8.13 (2H, m), 8.37 (1H, s).

1,4-Dimethyl-9-(2-methyl-1-propenyl)triptycene (25). This compound was similarly prepared from the anthracene and 3,6-dimethylanthranilic acid.[42] The product was purified by chromatography (hexane eluent) and recrystallized from methanol, mp 145.5—146.0 °C. The yield was 36%. Found: C, 93.11; H, 7.18%. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%. ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, s), 2.19 (3H, d, J=1.5 Hz), 2.41 (3H, s), 2.50 (3H, s), 5.61 (1H, s), 6.61 and 6.71 (2H, ABq, J=7.7 Hz), 6.84 (1H, br s), 6.95—7.02 (4H, m), 7.33—7.44 (4H, m).

Examination of Deuterium Incorporation in Formation of Compound 8. *sc*-**2** (354 mg) was shaken with a 5% solution of NaOD in D_2O and 10 mL of ether and the organic phase was treated as usual. The *sc*-amine-d_2 thus obtained showed the following ^{1}H NMR spectrum ($CDCl_3$, δ) which lacked the NH_2 proton signal: δ=2.08 (3H, s,), 2.09 (3H, s), 2.52 (3H, s), 2.58 (3H, s), 3.62 and 4.04 (2H, ABq, J=14.0 Hz), 5.58 (1H, s), 6.75 and 6.77 (2H, ABq, J=7.8 Hz), 6.91—7.02 (4H, m), 7.32—7.38 (2H, m), 7.87—7.93 (2H, m).

sc-**2**-d_2 (321 mg or 0.903 mmol) was dissolved in 8.0 mL of benzene, which had been shaken with D_2O and then distilled. To the solution was added 121 μL (0.904 mmol) of isopentyl nitrite and 102 μL (1.81 mmol) of acetic acid-d_4 and the whole was heated under reflux for 1 h. After the usual treatment, the hydrocarbon fraction (a mixture of **3**, **4**, **5**, **6**, and **8**) was obtained by TLC (1:2 hexane–dichloromethane) on silica gel. It was further treated with a Sanki centrifugal liquid–liquid partition chromatography (LLB) with a stationary phase of hexane and an eluent of acetonitrile. It was possible to separate the olefins (**3**, **4**, and **5**) from cyclic products (**6** and **8**). The mixture of the cyclic products was further submitted to chromatography (10:1 hexane–ether eluent) on silica gel which was impregnated with 10% silver nitrate. This procedure afforded a 15:1 mixture of **8** and **6**.

^{2}H NMR spectra of the 15:1 mixture of **8** and **6** in chloroform were recorded on a Bruker AMX-R400 spectrometer which operates at 61.4 MHz for ^{2}H. Since this machine was not equipped with a locking device, we have added ca. 6 mol per cent of *t*-butyl methyl-d_3 ketone and chloroform-*d* and the chemical shift values were adjusted by assuming that the chemical shifts of ^{1}H and ^{2}H in the same position of a compound are the same.[43] Although this may derive some errors but does not affect the conclusion.

We assume that at least one of the benzylic protons should appear at a lower field than the methylene protons at the 2-position. Thus we assign that the ^{2}H-signal at ca. δ=2.5 is due to 2-methylene protons. At this chemical shift, a signal of deuterium, if any, was buried in the background noise. Although the signal to noise ratio was not very good, the highest content of ^{2}H in **8** was estimated to be less than 10% of that of *t*-butyl methyl-d_3 ketone. Thus ^{2}H in 2-methylene protons in **8** must be less than 2%. The other part of the spectrum did not show any significant signal due to ^{2}H.

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