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1-Methoxyl Participation *vs*. Skeletal Rearrangement in Diazotization of 9-Aminomethyl-1,4-dimethoxytriptycene

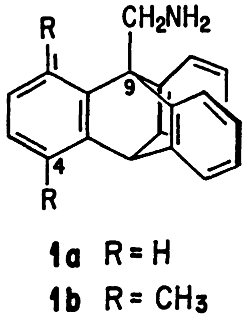
Gaku YAMAMOTO* and Michinori ŌKI
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo 113

The title reaction with nitrous acid in acetic acid gave 10-acetoxy-6,9-dimethoxyhomotriptycene (29%) and 9-chloromethyl-1,4-dimethoxytriptycene (20%) as major products, suggesting participation of the 1-methoxyl group or the C_9-C_{8a} bond depending on the rotational state of the diazonium ion.

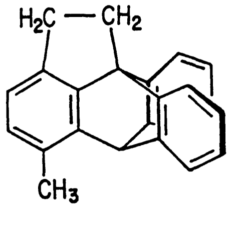
We recently reported that the reaction of 9-aminomethyl-1,4-dimethyltriptycene (**1b**) with nitrous acid in acetic acid gave a cyclized triptycene derivative **2** (46%) as a major product along with 1-(substituted methyl)-4,9-dimethyltriptycenes **3** (42%),$^{1)}$ in sharp contrast with the behavior shown by the *peri*-unsubstituted compound **1a** which gave exclusively the skeletally rearranged products **4**.$^{2)}$ This was ascribed primarily to the close proximity of the 1-methyl group to the reaction center in **1b** which enabled participation of the 1-methyl C-H bond.

A neighboring methoxyl group is widely recognized to participate in reactions as a potential nucleophile having oxygen lone pairs.$^{3)}$ In triptycene derivatives we found that the *peri*-methoxyl group efficiently reacts with the cationoid center at the β-position of the 9-substituent to give six-membered ethers.$^{4)}$ We now turned our attention to the effect of the *peri*-methoxyl group on the reaction of 9-aminomethyl-1,4-dimethoxytriptycene (**1c**) with nitrous acid in acetic acid as one of reactions occurring at the α-position of the 9-substituent.

Compound **1c** was synthesized from 9-anthracenecarboxaldehyde: Diels-Alder reaction with *p*-benzoquinone, isomerization of the adduct to the triptycene hydroquinone, O-methylation, conversion of the formyl group to its oxime, and reduction with lithium tetrahydridoaluminate gave **1c** in an overall yield of 48%.$^{5)}$ **1c** was



1a R=H
1b R=CH_3
1c R=OCH_3



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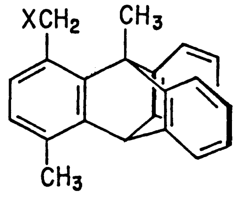

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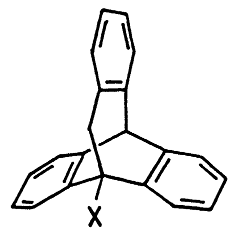
X=$OCOCH_3$, Cl



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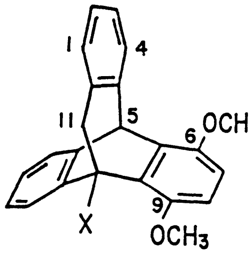
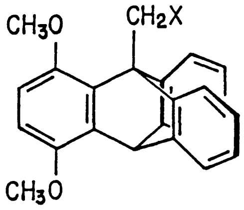
X=$OCOCH_3$, OH

converted to its hydrochloride which was treated in acetic acid with 10 equivalents of sodium nitrite at room temperature for 15 h. Although the reaction afforded a complex mixture of products, preparative gel permeation chromatography allowed us to isolate six compounds **5-10** (Table 1). A 10,11-dihydro-5,10-*o*-benzeno-5H-dibenzocycloheptene (homotriptycene) structure of **5** and **6** was deduced by the presence in the ^{1}H NMR spectra of a singlet at δ *ca.* 5.5 ascribed to the 5-methine proton and an AB-quartet at δ 3.2-3.6 ascribed to the 11-methylene group which clearly confirms that the compounds are the 6,9-dimethoxy derivatives but not the 1,4-dimethoxy ones with planar symmetry. The 9-(substituted methyl)-1,4-dimethoxytriptycene structure of **7-9** was confirmed by comparing the spectral data of **7** and **8** with the appropriate authentic samples.[6] ^{1}H NMR (an aromatic singlet at δ 7.213), MS, and IR spectroscopic analyses show the presence of a nitro group in **10** but its position is uncertain at this moment.

A plausible mechanism of the reaction of diazonium ion rotamers (*ap*/±*sc*-**11**) are shown in Scheme 1. We must here consider the rotational isomerism around the C_9-C_α bond in **11**. It plays an important role in determining the reaction paths, because participation of a neighboring group (either the 1-methoxyl group or the *o*-benzeno bridge of the triptycene skeleton) occurs when it is located in the rear



5 X = OCOCH$_3$
6 X = ONO$_2$



7 X = Cl
8 X = OCOCH$_3$
9 X = ONO$_2$

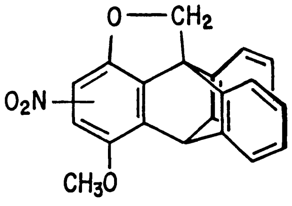


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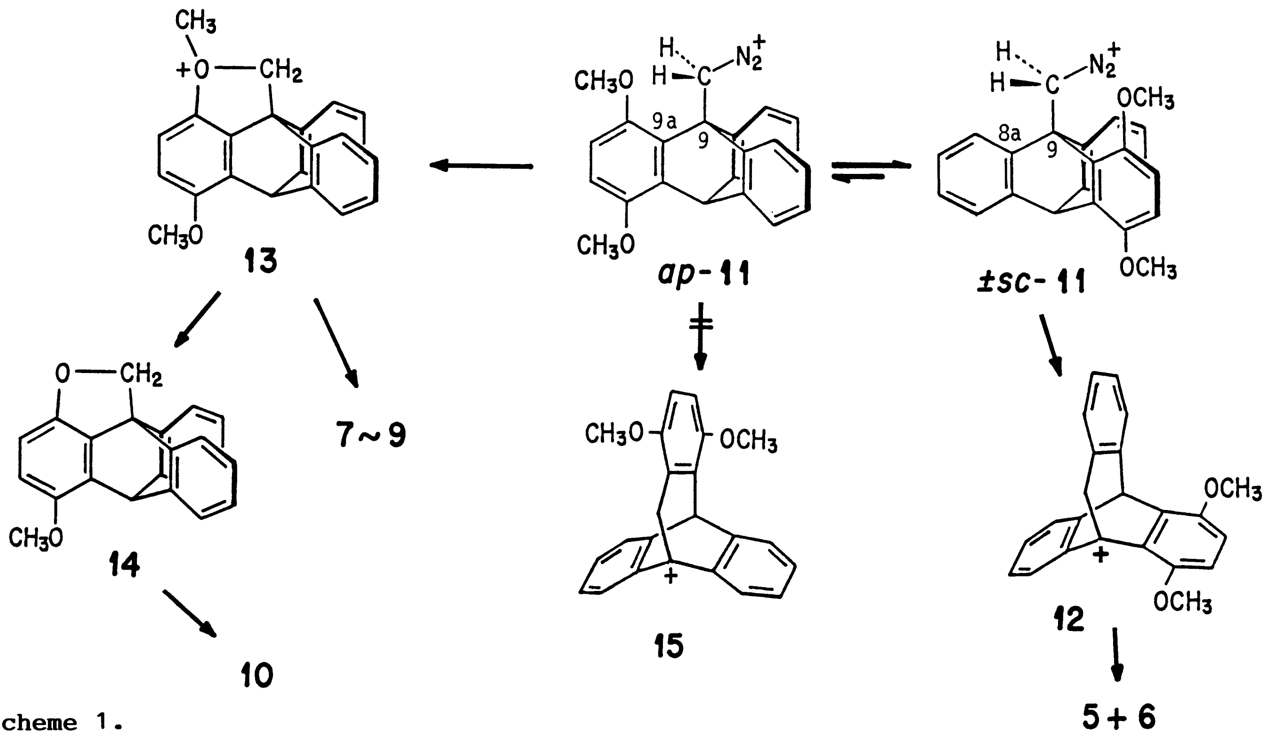
Table 1. Yields and Spectral Data of the Products.[a]

5	29%; MS: m/z 386(M$^+$, 92%), 344(100%), 329(77%); δ(H): 2.349(3H, s), 3.283 and 3.510(2H, AB-q, J=16.5 Hz), 3.780(3H, s), 3.802(3H, s), 5.500(1H, s), 6.696(2H, s), 6.84(1H, m), 6.95-7.05(2H, m), 7.10-7.40(5H, m).
6	8%; MS: m/z 389(M$^+$, 70%), 325(77%), 311(100%); IR: 1635, 1295 cm^{-1}; δ(H): 3.226 and 3.500(2H, AB-q, J=16.5 Hz), 3.780(3H, s), 3.837(3H, s), 5.531(1H, s), 6.749(2H, s), 6.86(1H, m), 7.0-7.1(2H, m), 7.2-7.45(5H, m).
7[b]	20%; MS: m/z 362(M$^+$, 96%), 282(100%); δ(H): 3.708(3H, br s), 3.766(3H, br s), 5.474(2H, br s), 5.858(1H, s), 6.430 and 6.480(2H, AB-q, J=8.8 Hz), 6.95-7.15(4H, m), 7.35-7.50(2H, m), 7.70-7.90(2H, m).
8[b]	5%; δ(H): 2.149(3H, s), 3.717(3H, br s), 3.792(3H, s), 5.888(1H, s), 5.8-6.1(2H, br), 6.4-6.6(2H, br), 6.9-7.1(4H, br), 7.3-7.5(4H, br).
9[b]	7%; MS: m/z 389(M$^+$, 100%); IR: 1632, 1285 cm^{-1}; δ(H): 3.725(3H, br s), 3.806(3H, s), 5.892(1H, s), 6.15-6.45(2H, br), 6.518 and 6.566(2H, AB-q, J=8.9 Hz), 6.90-7.15(4H, m), 7.30-7.50(4H, m).
10	6%; MS: m/z 357(M$^+$, 100%); IR: 1520, 1330 cm^{-1}; δ(H): 3.873(3H, s), 5.831(1H, s), 5.926(2H, s), 7.00-7.15(4H, m), 7.213(1H, s), 7.30-7.50(4H, m).

a) IR: Nujol mull. ^{1}H NMR: 270 MHz, $CDCl_3$, *ca.* 20 °C. Satisfactory elemental analyses were obtained for **5**, **7**, and **8**. b) Some of the ^{1}H NMR signals are broadened because of slowing-down of rotation around the C_9-C_α bond.



Scheme 1.

of the departing nitrogen molecule of the diazonium species. The homotriptycene derivatives 5 and **6**[7)] must have been derived from the homotriptycyl cation **12**, which in turn should be formed by participation of the C_{8a}-C_9 bond in ±sc-**11**. Compounds **7-10** should be derived from ap-**11**: The oxonium ion **13** will be formed as soon as ap-**11** is generated because the 1-methoxyl group is located nicely in the rear of the departing nitrogen and very close to the incipient cation. Attack of nucleophiles on the methylene carbon of **13** will cleave the CH_2-O bond to give **7-9**, while nucleophilic attack on the methyl carbon will afford the dihydrobenzofuran derivative **14** which is further nitrated to **10**. Preferential cleavage of the O-CH_2 bond over the O-CH_3 bond may be due to the large strain of the five-membered ring fused with the triptycene skeleton.[8)] Since the peri-unsubstituted compound **1a** did not afford the direct displacement products at all,[2)] **7-9** can not be formed by direct attack of nucleophiles on ap/±sc-**11**. Judging from the absence of 1,4-dimethoxyhomotriptycene derivatives in the reaction mixture, we conclude that the C_9-C_{9a} bond participation in ap-**11** to give 1,4-dimethoxy-10-homotriptycyl cation **15** does not compete with the 1-methoxyl participation. This suggests that the rearrangement ±sc-**11** → **12** is energetically less favorable than the oxonium ion formation ap-**11** → **13**, since the Wagner-Meerwein rearrangements, ap-**11** → **15** and ±sc-**11** → **12**, can be assumed to have similar activation energies. Formation of products derived from **12** and from **13** in almost equal amounts (37% vs. 38%) indicates that two rotamers of the diazonium ion (ap/±sc-**11**) exist in comparable amounts and the interconversion between them is slow relative to their decay. If the interconversion were fast, the products derived from **13** should have been more abundant. While no pertinent data for the decay rates of **11** rotamers are available, the rotational barriers around the C_9-C_α bond in **11** is inferred to be of the order of 15 kcal/mol.5) ^{1}H NMR spectrum of **1c** in $CDCl_3$ at -30 °C revealed the predominance of the ±sc rotamer.5) Although many factors affect the rotamer populations, it may be reasonable to assume that the hydrochloride salt of **1c** exists predominantly in the ±sc rotamer in the present reaction media and the rotamer populations are retained during the reaction course to the extent that the diazonium ion rotamers exist in almost equal amounts.9)

The present case represents an example of violation of the classical Curtin-Hammett conditions:10) the interconversion between the reactive conformers is sufficiently slow relative to the product-forming steps, although the former is not slow enough for the respective rotamers to be isolated.11)

References

1) G. Yamamoto and M. Ōki, Chem. Lett., 1987, 1163.

2) S. J. Cristol and D. K. Pennelle, J. Org. Chem., 35, 2357 (1970).

3) B. Capon, Quart. Rev., 18, 45 (1964).

4) G. Izumi, S. Hatakeyama, N. Nakamura, and M. Ōki, Bull. Chem. Soc. Jpn., 54, 258 (1981).

5) **1c**: mp 184-186 °C; ^{1}H NMR($CDCl_3$, 270 MHz): δ ca. 3.3(2H, br s), 3.77(3H, s), 3.81(3H, s), 4.0-4.9(2H, br), 5.86(1H, s), 6.55(2H, br s), 6.8-7.2(4H, m), 7.2-8.0(4H, br m); signals are broadened at ambient temperature due to slow rotation around the C_9-C_α bond. The spectrum at -30 °C showed two sets of signals due to two rotamers, ap and ±sc, in a ratio of 14:86. The dynamic NMR study gave the free energy of activation of 14.9 kcal/mol at 20 °C for the ap to ±sc process.

6) Y. Tamura and M. Ōki, in preparation.

7) Formation of nitrates is often observed in nitrous acid deamination of amines. See for example: R. H. White and D. T. Woodcock, "The Chemistry of the Amino Group," ed by S. Patai, Interscience (1968), Chap. 8.

8) In the solvolyses of 2-(o-methoxyphenyl)-2-methylpropyl tosylate, the O-CH_3 cleavage in the intermediate oxonium ion is preferred over the O-CH_2 one: R. Heck, J. Corse, E. Grunwald, and S. Winstein, J. Am. Chem. Soc., 79, 3278 (1957); S. Winstein, E. Allred, R. Heck, and R. Glick, Tetrahedron, 3, 1 (1958). If we take into account the well-known high reluctance of a neopentyl-type primary carbon to participate in an S_N2 reaction, it might be an alternative to postulate the existence of the open 9-triptycylmethyl cation, stabilized by the neighboring methoxyl group, in equilibrium with **13**.

9) It is generally accepted7) that the rate-determining step of diazotization of amines is formation of a nitrosamine and the following successive steps occur very rapidly.

10) See for example: J. I. Seeman, Chem. Rev., 83, 83 (1983); J. Chem. Educ., 63, 42 (1986).

11) Differential reactivities of stable rotamers have been studied: M. Ōki, Acc. Chem. Res., 17, 154 (1984).

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