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Diazotization of 2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propylamine Rotamers. A Consequence of Participation of 1-Chloro Substituent during the Formation of Alkyl Cation in the sc-Isomer[1)]

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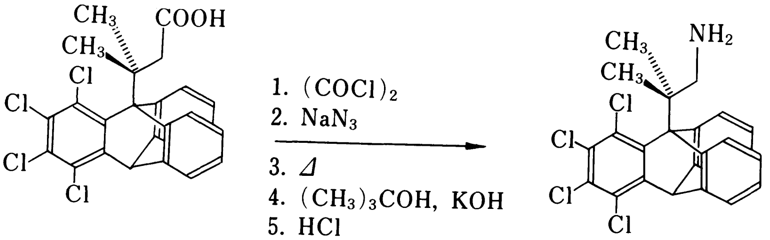
Diazotization of the ap form of the title compound in benzene with isopentyl nitrite in the presence of acetic acid afforded a mixture of olefins, which were expected from deprotonation reactions of the cation formed by the Wagner-Meerwein rearrangement, while the sc isomer afforded 2-methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl acetate. Participation of the 1-chloro group in stabilization of the cation formed by diazotization was invoked.

While enhancement of the reactivity of the sc isomer in a cation-forming reaction in the presence of a chloro substituent in proximity of the cation-forming site has been reported[2)] as one of the examples in the differences in reactivities of rotamers,[3)] the reaction afforded the same mixture with that from a reaction which does not exhibit the chloro-participation. If we can find a reaction that gives different product(s) due to the chloro-participation from that formed in the absence of the participation, it will be intriguing not only on the basis of the product formation but also on a possibility that could give further insight into the reaction mechanisms.

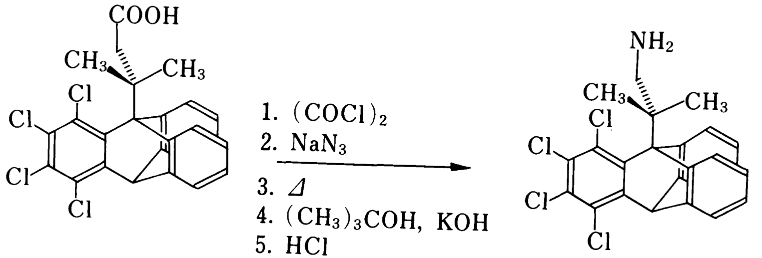
We chose the chloro-participation for the following reasons. Firstly, if a strong participation is expected, that might give product(s) of a true reaction rather than those derived from the participation, like the formation of cyclic ethers from 1-methoxytriptycene derivatives.[4)] Secondly the fate of a cation is well known,[2)] if it is formed in the absence of participation, and the product distribution could be compared with that reported. In this paper, we wish to report differences observed in the diazotization of the rotamers of 2-methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propylamine (1).

The amine rotamers (1) were synthesized from the corresponding carboxylic acid (2) rotamers:[5)] the acid was converted to the azide which was converted to isocyanide by the Curtius rearrangement.[6)] Conversion of the isocyanide to the amine caused difficulties that could be overcome by the use of potassium hydroxide in t-butyl alcohol.

The diazotization of the amine (1) was carried out with the use of a little excess of acetic acid in benzene with the aid of isopentyl nitrite at 80 °C. The



ap-**2** *ap*-**1**



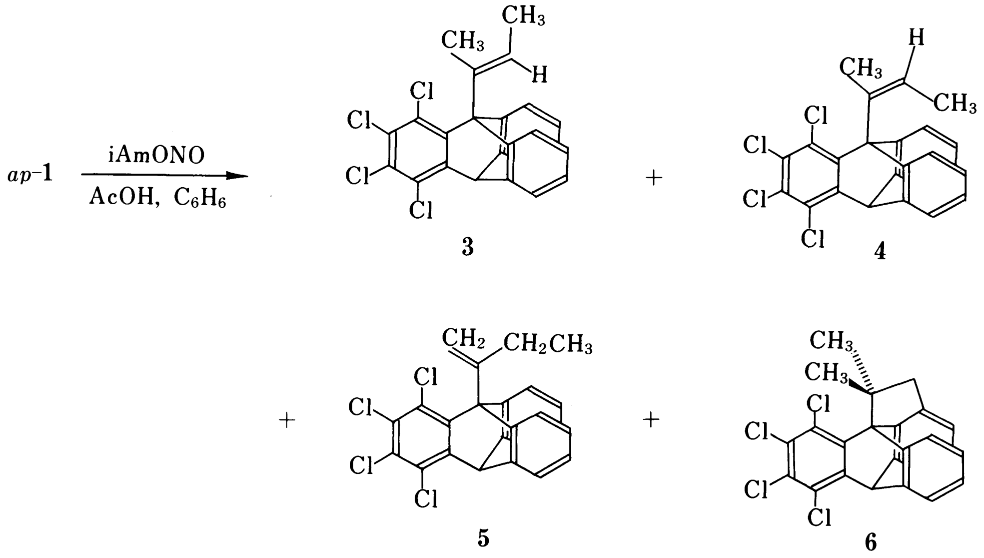
sc-**2** *sc*-**1**

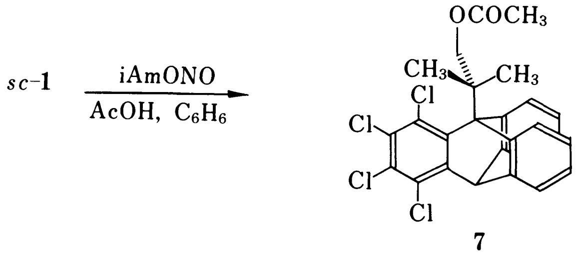
products were submitted to TLC on silica gel and the following products were identified by ^{1}H NMR spectra in the case of the ap-isomer: (E)-1-(1,2,3,4-tetrachloro-9-triptycyl)-2-butene (**3**) (70%), (Z)-isomer (**4**) (5%), 2-(1,2,3,4-tetrachloro-9-triptycyl)-1-butene (**5**) (10%) and 1,1-dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene (**6**) (10%). The major product was **3**. In the case of sc-isomer, however, none of these products was detected but there was obtained a product in 90% yield. The structure of the new product was assigned to 2-methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl acetate (**7**) on the ground of spectroscopic data and mechanistic considerations.

The formation of the olefins and the cyclized product (**6**) can be rationalized, when a cation (**8**) is formed as a result of diazotization,$^{6)}$ as follows. When the cation (**8**) attacks the peri-position of the triptycene skeleton before rearrangement, the product should be **6**. The cation (**8**) may undergo the Wagner-Meerwein rearrangement, because the reaction is known to be typical for neopentyl-type cations.$^{7)}$ The cation (**9**) thus poroduced will yield the olefins, **3**, **4**, and **5**, on deprotonation. The major formation of **3** can be understood as a result of kinetic control, because the transition state for the formation of **4** should be energy-requiring due to the steric effect.

The less formation of **5** should be attributed to the transition state energy as well, as is known as the Saytzeff's rule.$^{9)}$ It is interesting to note the presence of **5**, however, because this compound was not detected in the case of ionization of the corresponding chloro-compound with the aid of Lewis acids.$^{2)}$ We wish to attribute this difference in the presence or absence of acids. In the present case, the acid was acetic acid and was used only a little excessively (2.5 mol of acid for 1 mol of amine), while in the past the Lewis acid was used in great excess. Thus it is possible that the excess of the acid catalyzed the isomerization of olefins to produce the most stable one.

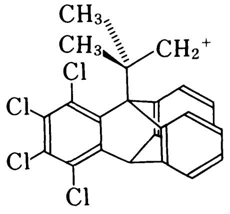
The formation of the ester (**7**) must occur by the attack of the acetate anion



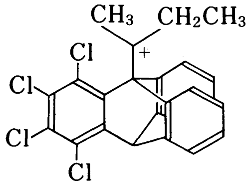


present in the system on the cation before the Wagner-Meerwein rearrangement takes place. That means that the cation (sc-8) has a longer life than the ap-isomer (ap-8). This stabilization must be caused by the participation of the chloro group in proximity, as is known as anchimeric assistance in solvolytic reactions.10) Absence of any rearranged products is the indication that the cation (sc-8) is formed distinctly and is frozen as such until it undergoes the electrophilic reaction to form 7.

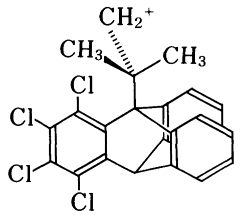
Above discussion implies that the rearrangement of the carbenium ion sc-8 to 9 competes with the nucleophilic attack. In the case of acetate ion, the nucleophilicity of the anion is high enough to overcome the rearrangement. Then it leads to a prediction that, if the nucleophilicity of an anion present in the



ap-8



9



sc-8

system is low enough, sc-1 should give olefins and possibly the cyclized product on diazotization. Indeed in the presence of trifluoroacetic acid, diazotization of sc-1 in benzene afforded small amounts of **3**, **4**, 5, and **6**, in addition to 70% trifluoroacetoxy compound corresponding to **7**.

Solvent effects on the fate of the cation is very important as is common in other diazotization reactions.7) When the same reaction was run in acetic acid, sc-1 afforded no detectable acetate (**7**), but olefins (3 and **4**) were obtained. We tentatively attribute the results to the difference in the solvation of the intervening ion pair due to the high polarity of acetic acid which gives more stabilization due to solvation of the ion pair than the chloro-participation.11) Under these circumstances, the migration of the alkyl group will become possible.

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