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INTRAMOLECULAR INTERACTION BETWEEN METHOXYL AND ACYLOXYMETHYL GROUPS IN TRIPTYCENE SYSTEMS

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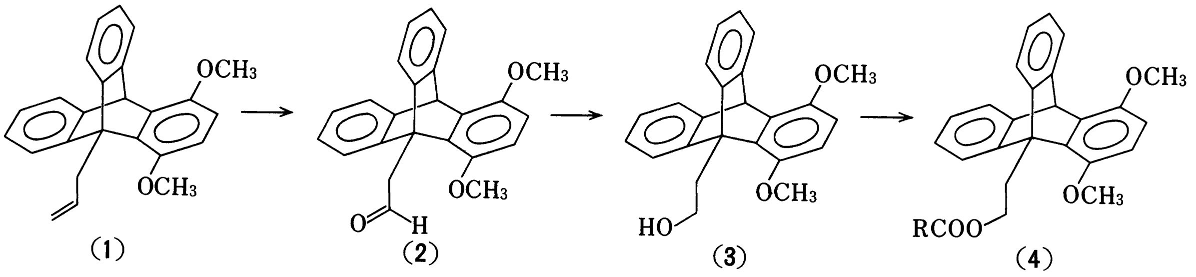
Populations of conformers of 9-(2-acyloxyethyl)-1,4-dimethoxytriptycene suggest that there is an attractive interaction between the acyloxymethyl and the methoxyl groups. The effects of the electronegativities of the acyl group upon the distribution of conformers and the relation between the interaction and S_N2 reactions are discussed.

A surprising difference has been found in the reactivities of the ±sc and ap rotamers of 9-(2-chloro-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene:1) the ±sc form reacts much faster than the ap form in a Lewis acid-catalyzed reaction. The results suggest that there may be a kind of interaction between the chloro and the chloromethyl groups in proximity which facilitates the reaction of the ±sc form: this interaction can well be attractive. Since we have been able to show the existence of an attractive interaction between the group with lone pairs of electrons and the carbonyl moiety,2) we hoped that, if the attractive interaction exists between the chloro and the chloromethyl groups, it should be reflected to the populations of rotamers as well.

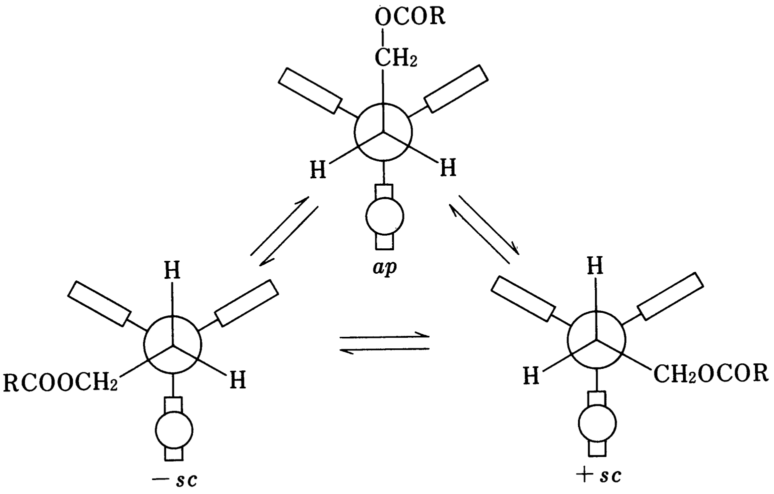
Preliminary experiments revealed that, contrary to the expectation, 9-(2-chloroethyl)-1,2,3,4-tetrachlorotriptycene existed solely as the ap-isomer. The results might be caused by that, because of the weakness, the interaction could not overcome the repulsive interaction between the chloro and the chloromethyl groups. Then we tried to prepare 9-(2-chloroethyl)-1,4-dimethoxytriptycene from the corresponding alcohol and thionyl chloride, because the methoxyl group is a better electron-donor than the chloro group. Again an unexpected phenomenon occurred: a cyclic ether is formed,3) instead of the desired compound. The reason for this unexpected result was thought to be a very strong interaction between the methoxyl group and a cationoid formed by the reaction between the alcohol and thionyl chloride.4) Therefore, we decided to use the methoxyl group in the peri-position and acyloxymethyl groups, which are less electron demanding than the cationoid formed during the reaction, at the bridgehead to see the population ratios of the rotamers. This paper reports the results of the investigation.

The syntheses of the compounds employed in this investigation were carried out by reduction of 9-formylmethyl-1,4-dimethoxytriptycene (2), which was prepared by ozonolysis of a 9-allyl compound (1), to the corresponding alcohol (3) followed by acylation.



(1) (2) (3) (4)

^{1}H NMR spectra were obtained on a Hitachi R-20B spectrometer. The signal due to 1-CH_2 protons of the 2-acyloxyethyl group splits into a singlet and an AB quartet at low temperatures on irradiation of the 2-CH_2 protons. The former corresponds to the ap form and the latter the ±sc form, as are clear from the Newman projections.



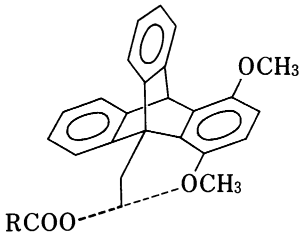
In practice, however, the methoxyl signals overlap with the higher field signal of the AB protons of the ±sc form and a signal due to the ap form: the overlap makes the error in population analysis large, at best. Thus we prepared some triptycenes (4) with the methoxyl groups completely deuterated. This work fortunately revealed that the signals due to protons of the dimethoxybenzo group could be used for the population analysis: a signal at ca. δ 6.5 at room temperature, which appears apart from other aromatic proton signals, splits into a doublet at low temperatures and the signal at a higher field of the doublet corresponds to the ap form and that at a lower field to the ±sc form. All the population ratios obtained from these signals agreed well with those obtained from the singlets and the AB quartets due to the 1-CH_2 group. The results are shown in Table 1 together with some pertinent data.

Table 1 Population Ratios (±sc/ap) about the C_9-C_{subst} Bond of 4 in $CDCl_3$ and pKa's of the Corresponding Carboxylic Acids

R	±sc/ap	Temperature/°C	pKa[5)
CH_3	1.5	-45	4.75
C_6H_5	1.7	-50	4.20
$ClCH_2$	2.0	-45	2.87
Cl_2CH	2.5	-45	1.29
Cl_3C	3.0	-50	-0.08
F_3C	3.0	-50	0.23

Inspection of the data in Table 1 reveals that, the smaller the pKa of the acid corresponding to the acyloxy group, the larger the ±sc/ap value. Since the ability as a leaving group is reflected by the pKa value,6) the results may be expressed as that the better the leaving ability of the acyloxy group, the larger the ±sc/ap value. Although 9-ethyl-1,4-dimethoxytriptycene is known to exist as an almost 1:1 mixture of ±sc and ap forms,7) the general tendency of favoring the ±sc form on the increase of the electronegativity of the acyloxy group is indicative of the presence of some kind of attractive interaction between the substituents concerned, where the methoxyl group acts as an electron donor and the group involving the acyloxy group as an electron acceptor.

We wish to attribute this attractive force to the interaction between the σ^* orbital, which involves the C-O bond to a large extent, and the n orbital involving the oxygen of the methoxyl group: if the electronegativity of the acyloxy group increases, the σ^* orbital will effectively be lowered in its energy to become more efficient for the interaction. The interaction is schematically given by 5.



(5)

It may be argued that the attractive interaction occurs between the methoxyl group and the carbonyl moiety of the acyloxy group, as are found in other cases.2,8) If it were the case, however, the ring formed by the interaction would be 8-membered. This will be unfavorable both from entropy and from steric grounds. It may further be argued that the phenomenon is caused by the formation of C-H···O hydrogen bond as was suggested by Hayami and other workers in the Finkelstein reactions.9) However, we are tempted to attribute it to the interaction cited above for the following reasons.

S_N2 reactions have been studied in the gas phase by high pressure mass spectrometry[10)] and by ion cyclotron resonance.[11)] Both groups of workers agree in that a complex is formed between an organic halide and a nucleophile. The most noteworthy point is that carbon tetrachloride[10a)] and tert-butyl bromide[10b)] form the complex. If the driving force for the formation of the complex were the hydrogen bond, these compounds would have not formed the complex. Since we are observing the phenomenon in a relatively nonpolar solvent and the solvent intervention will be minimal due to the steric effect of the system, the phenomenon will best be approximated by the model in the gas phase.

If we admit that the attractive interaction takes place between the methoxyl and the acyloxymethyl group, as in 5, we notice that we are dealing with an incipient transition state for S_N2 reactions. Our finding presented here may supplement the argument on the mechanism for S_N2 reactions by providing the data in a solvent of low polarity. Further study on this kind of interaction should shed light for the understanding of reactions which are fundamental in organic chemistry.

References

1) H. Kikuchi, T. Mitsuhashi, and M. Ōki, Chem. Lett., 1980, 209.
2) M. Ōki, G. Izumi, G. Yamamoto, and N. Nakamura, Chem. Lett., 1980, 213.
3) G. Izumi, S. Hatakeyama, and M. Ōki, unpublished work.
4) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, "Ions and Ion pairs in Solvolysis Reactions" in " Ions and Ion Pairs in Organic Reactions," ed. by M. Szwarc, John Wiley & Sons, New York (1974), Vol. 2, pp. 350-351.
5) "Constants of Organic Compounds," ed. by M. Kotake, Asakura Publishing Co., Tokyo (1963).
6) L. P. Hammett and H. L. Pfluger, J. Am. Chem. Soc., 55, 4079 (1933).
7) H. Nakanishi and O. Yamamoto, Bull. Chem. Soc. Jpn., 51, 1777 (1978).
8) M. Kaftory and J. D. Dunitz, Acta Cryst., B31, 2917 (1975).
9) J. Hayami, T. Koyanagi, N. Hihara, and A. Kaji, Bull. Chem. Soc. Jpn., 51, 891 (1978) and papers cited therein.
10) a) R. C. Dougherty, J. Dalton, and J. D. Roberts, Org. Mass Spectrom., 8, 77 (1974): b) R. C. Dougherty, ibid., 85.
11) W. M. Olmstead and J. I. Brauman, J. Am. Chem. Soc., 99, 4219 (1977).

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