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ON THE REACTIVITY OF 9-CHLORO-9-PHENYL-BICYCLO(3. 3. I)NONANE

L. Baiocchi, M. Giannangeli and G. Palazzo
Laboratorio Ricerche Angelini - Rome - Italy

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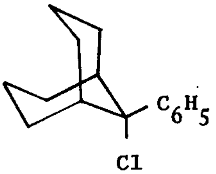
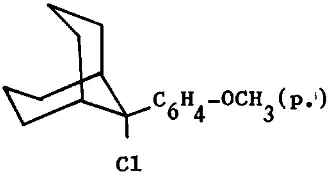
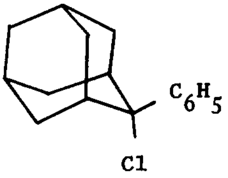
The unexpected high reactivity of 9-chloro-9-phenyl-bicyclo(3. 3. I)nonane (I) towards substances capable of forming hydrogen bonds (water, alcohols (1), phenols, acids, amides, aromatic amines) and its remarkable inertia towards ammonia and aliphatic amines led us to compare the behaviour of (I), (II), (III) and trityl chloride (IV) in some solvolytic reactions.



I (Ph-B-Cl)



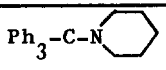
II (A-B-Cl)



III (Ad-Cl)

The following table shows the composition of the products obtained from 0, 05M solutions of the four substrates at room temperature and after completion of reaction (a week in the first case, one hour in the second).

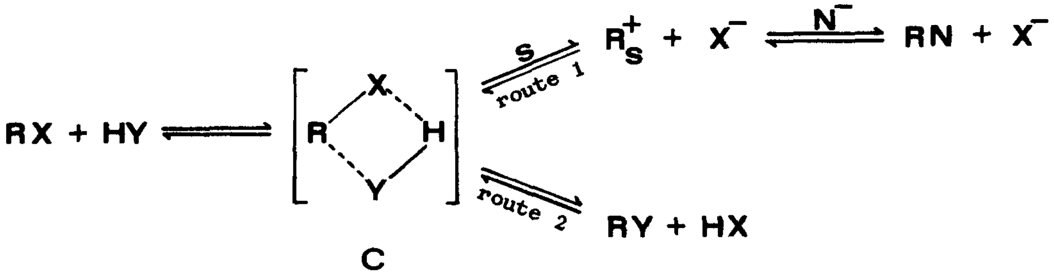
TABLE

	(I)	(II)	(III)	(IV)
Methanol piperidine equimolecular mixture	Ph-B-OCH_3	A-B-OCH_3	Ad-O-CH_3	 $\text{Ph}_3\text{-C-N}$
0,05M NaN_3 in methanol	Ph-B-OCH_3	A-B-OCH_3	Ad-O-CH_3	$\text{Ph}_3\text{-C-OCH}_3$ (18%) $\text{Ph}_3\text{-C-N}_3$ (82%)

Actually the relative alcoholysis rates (K) change in the order:

$$K(II) > K(IV) > K(I) > K(III)$$

These data clearly point out that the quality of the products obtained in said reactions does not depend, as expected, on the solvolysis rates of the four substances, but on their structures. Furthermore, it should be noted that the solvation of the carbonium ion corresponding to (I) is certainly hindered by the same steric factors which are operating in the case of 2-adamantyl ion (2), and that the dissociation of (IV) takes place in solvents, of even high dieletric constant, only in the presence of catalytic quantities of hydroxylated substances (3). The simplest scheme which takes into account all the above considered facts is the following one :



In this scheme it is admitted that, in solvolysis of tertiary substrates, complex (C) is always formed (4). (C) will then evolve according to the nature of substrate and reaction medium: when R^+ is easily solvated, HY acts as a mere catalyst as regards the formation of (C) and its subsequent dissociation, brought about by the solvent. Stable carbonium ions are formed which preferably react with the most nucleophilic component present.

When steric reasons prevent the carbonium ion solvation, (C) is not dissociated by the solvent, but an internal reaction takes place. We wish to emphasize what appears to be the main characteristic of this mechanism. HY has no more a mere catalytic action but, for each activated molecule (i. e. for each molecule which is able to react) a HY molecule is activated in turn.

Intermediate behaviours are, of course, possible.

The same trityl chloride, for instance, reacts with an equimolecular mixture of methanol and piperidine, giving appreciable quantities of trityl methyl ether when the reaction is carried out in a poorly solvating medium as carbon tetrachloride. On the other hand hydrolysis of (II) (where there is a substituent involving a remarkable charge dispersion) in a mixture of water and acetone in the presence of sodium azide leads to the formation of remarkable quantities of azide (beside the corresponding alcohol) even if in smaller quantities than those obtained from trityl chloride, i. e. not reflecting the solvolysis rates.

The definition of the two routes implies racemization for the first one and retention of configuration for the second.

REFERENCES

1) Ethanolysis data were reported by same authors, Tetrahedron Letters 5025 (1970)
2) P. v. R. Schleyer, J. Am. Chem. Soc. 92, 2540, 2542, 2544 (1970)
3) A. Streitwieser, Chem. Rev. 56, 912 (1956)
4) B. Tchoubar, Bull. Soc. Chem. Fr. 2069 (1964)