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ETHANOLYSIS OF TERTIARY 9-CHLORO-BICYCLO(3.3.1)NONANES

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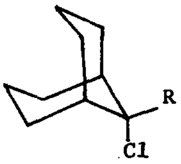
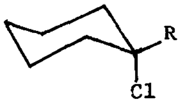
The solvolysis rates of a series of tertiary α-aryl-substituted cycloalkyl chlorides were recently determined (1). This series did not include 9-substituted-bicyclo(3.3.1)nonanes, the only available data being on the acetolysis of secondary tosylates, from which many rearranged products are obtained (2,3). We have therefore synthesized the tertiary chlorides Ia, b, c, d and studied their ethanolysis.

9-Chloro-9-methyl-bicyclo(3.3.1)nonane Ia (m.p. 130°) is readily obtained by heating the corresponding carbinol (m.p. 170°) with concentrated hydrogen chloride. The yield is excellent and no rearrangement is observed. In a similar way Ib (m.p. 109°), Ic (m.p. 82°) and Id (m.p.86°) can be prepared from the corresponding carbinols (m.p. 84-88°, 65°, 108-10° respectively) which, in turn, are obtained by Grignard reactions of bicyclo(3.3.1)nonan-9-one with suitable aryl- or alkyl-magnesium halides. Overall yields are high and satisfactory analytical data for all new compounds are obtained.

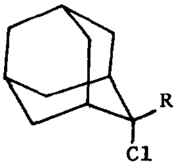
The ethanolysis at 25° of Ia, b, c, d proceeds very rapidly and yields the corresponding ethers entirely unrearranged. The comparison between the K values of these substrates and those of closely correlated products needs some consideration.



I a,b,c,d



II a,b



III b

a: $R=CH_3$
b: $R=C_6H_5$
c: $R=p.Cl-C_6H_4$
d: $R=p.CH_3O-C_6H_4$

TABLE I(°)

compound	$10^5K(sec^{-1})$	
	sol.0.05 M absolute ethanol	sol. 0.05 M 80% ethanol
Ia	0.135	7.95
Ib	480	
Ic	148	
Id	> 1000	
IIa		0.295(4)
IIb	5.9(5)	
IIIb	179	

(°) K were determined according to G.Baddeley and al. (5)

In I an axial chlorine atom is always present and it is also present in more than 90% of molecules II, as calculated from the conformational energies of the substituents (6). Moreover in I the R substituent is in an axial position with respect to the second cyclohexane ring. The higher reaction rate of Ia and Ib as compared to IIa and IIb can probably find an exhaustive explanation in the relief of repulsion due to the two "syn" axial hydrogen atoms which occurs when passing from the ground to the transition state. The extent of this repulsion may be estimated by noting that the interactions between the axial methyl or phenyl group and the syn-axial hydrogens should be the same as the corresponding interactions of axial methyl or phenyl in cyclohexane. In fact the reaction rate ratios IIa/Ia and IIb/Ib (26.8 and 81.5 respectively) correspond to $-\Delta G°$ values of 1.9 and 2.7 K cal/mole respectively, these values being in perfect agreement with the already known ones for the conformational energies for a methyl and a phenyl group in cyclohexane, which may represent just a measure of such repulsion.

However formation of the quasi-trigonal transition state with preferred 120° angles is obviously resisted more in the case of 9-substituted derivatives of bicyclo (3.3.1)nonane than in the case of the corresponding cyclohexanes, suggesting that a greater degree of strain must be present in the transition state of bicyclo(3.3.1)nonanes. As an indirect measure of this strain a relationship with the $\nu_{C=0}$ values of the corresponding ketones IR spectra (in CCl_4 solution) has been proposed (7). As a matter of fact we found a $\nu_{C=0}$=1726 cm^{-1} for bicyclo(3.3.1)nonan-9-one, this value being remarkably higher than the one reported for cyclohexanone ($\nu_{C=0}$=1718 cm^{-1}) and very near to the one corresponding to adamantanone ($\nu_{C=0}$=1727 cm^{-1}) (8). Since in the case of adamantane an angle strain is actually present (2), the same should also apply for bicyclo (3.3.1)nonane.

On the other hand it is well known that bicyclo(3.3.1)nonanes generally exist in the double chair form (9). Our molecules I, as well, show the typical IR absorption at 2990 cm^{-1} characteristic of the interaction between the hydrogen atoms in position 3 and 7. This interaction causes the corresponding carbon atoms to move further away from each other with a distortion of the ideal chair conformation. As a consequence, the compression of the two "syn" hydrogen atoms facing the axial substituent is greater than the one existing in an ideal geometric system such as, e.g., in adamantanone (compare the K values for Ib and IIIb).

The two effects considered seem therefore to compensate each other.

The influence of a p.chloro and p.methoxy substituent as in compounds Ic and Id is within the well known effects of benzene ring substituents.

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KEY WORDS

Conformational energy

Solvolysis

Tertiary chlorides

Angle strain

Cycloalkanones