The yield of pure, recrystallized (water–ethanol) peptides is 85–90%.

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Dipole Moments of Central-Atom Molecules

BY A. D. FRANKLIN

The general equation for the mean square dipole moment of a molecule with a rigid skeleton given by Eyring[1] may be solved in detail for the case of a central atom to which several different rotating polar groups are attached. An example is ethyl orthocarbonate. The observed moment should correspond to the square root of this mean square moment.

Eyring's equation in this case reduces to

$$\overline{\mu^2} = m^2 + \sum_i s_i^2 + 2\sum_i \overline{(\vec{m}\cdot\vec{s_i})} + 2\sum_{i>j} \overline{(\vec{s_i}\cdot\vec{s_j})}$$

where the subscript i refers to the i^{th} group, $\vec{m} = \sum_i(\vec{m_i} + \vec{r_i})$, $\vec{m_i}$ is the moment associated with the bond joining the group to the central atom, and $\vec{r_i}$ and $\vec{s_i}$ are the components of the group moment along and perpendicular to this bond, respectively. The averages, which drop out for the case of free rotation, are to be taken over the various orientations of the polar groups.

In Table I are gathered the observed moments and those calculated assuming free rotation for several examples of this type of molecule.

TABLE I

Et represents the ethyl group; Me the methyl; and Ph the phenyl group.

Compound	Debye units Calcd.	Obsd.
$(EtO)_3SiH$	2.8	1.78[2]
$(EtO)_4Ti$	2.1	1.41[3]
$(EtO)_4Si$	2.1	1.70[4]
$(EtO)_4C$	2.1	1.1[5]
$(MeO)_4C$	2.1	0.8[5]
$(EtO)_3TiCl$	1.8	2.87[3]
$(PhO)TiCl_3$	1.3	2.97[3]
$(CH_2Cl)_4C$	2.8	0[5]
$(CH_2Br)_4C$	2.6	0[5]
$(CH_2I)_4C$	2.3	0[5]
$(EtO)_2SO$	3.0	2.96[4]
$(EtO)_3PO$	2.9	3.07[4]

All bond angles about the C, Si, Ti, P and O atoms were assumed to be tetrahedral. The configuration of $(EtO)_2SO$ was taken as identical to $SOCl_2$.[6] Bond moments were either taken from Smyth and co-workers[7,8,9] or else calculated from Pauling's[10] electronegativity values, and the equations given by Hannay and Smyth.[11]

There is no agreement evident in the table, the observed values lying below the calculated in most cases. It has been suggested that this trend is due to an increase in the bond angle at the polar group.[3,12] Although this may occur with the Ti and Si compounds, it is not likely to be the cause of the zero moment observed with the neopentyl compounds. Since it can readily be shown that dipole–dipole interaction alone is of the same order as *kT*, and combined with steric hindrance would tend to exclude configurations with large moments, sufficient reason for the low moments can be found in lack of free rotation. Yamasaki, *et al.*,[13] came to the same conclusion regarding $(MeO)_4Si$ on the basis of electron diffraction studies.

Until more is known about the interactions between rotating groups upon the same molecule, it can only be concluded that calculations based upon free rotation in these molecules are unsatisfactory, and although the dipole results do not rule out the possibility of a wider oxygen bond angle in the Ti and Si molecules, neither do they give any real information on this point.

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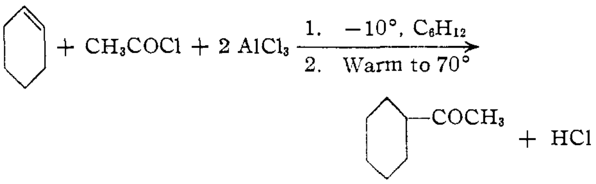
A Rearrangement in the Nenitzescu Reaction of Cycloheptene with Acetyl Chloride and Aluminum Chloride

BY S. L. FRIESS AND REX PINSON, JR.

In the course of preparation of a series of acetylcyclanes an attempt was made to synthesize methyl cycloheptyl ketone (I) using the acylation procedure of Nenitzescu and Cioranescu.[1] In the general procedure for the reaction, two moles of aluminum chloride are added in portions to a mixture of the olefin and acid chloride in cyclohexane solvent at about −10°, and upon warming slowly to 70°, HCl is evolved and the saturated ketone is obtained. For example



Nenitzescu found that the reaction progresses quite satisfactorily for 5- and 6-membered cyclic olefins, with the solvent acting as the ultimate hydrogen donor for the production of the saturated

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