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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[1] H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[2] H. Spauschus, A. Mills, J. Scott and C. MacKenzie, THIS JOURNAL, **72**, 1377 (1950).

[3] R. Crowe and C. Caughlan, *ibid.*, **72**, 1694 (1950).

[4] W. Svirbely and J. Lander, *ibid.*, **70**, 4121 (1948).

[5] L. Ebert, R. Eisenschitz and H. V. Hartel, *Naturwissenschaften*, **15**, 668 (1927).

[6] K. Palmer, THIS JOURNAL, **60**, 2360 (1938).

[7] C. P. Smyth and K. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

[8] C. P. Smyth, G. Lewis, A. Grossmann and F. Jennings, THIS JOURNAL, **62**, 1219 (1940).

[9] C. P. Smyth, *ibid.*, **60**, 183 (1938).

[10] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939, p. 64.

[11] N. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 171 (1946).

[12] R. Sauer and D. Mead, *ibid.*, **68**, 1794 (1946).

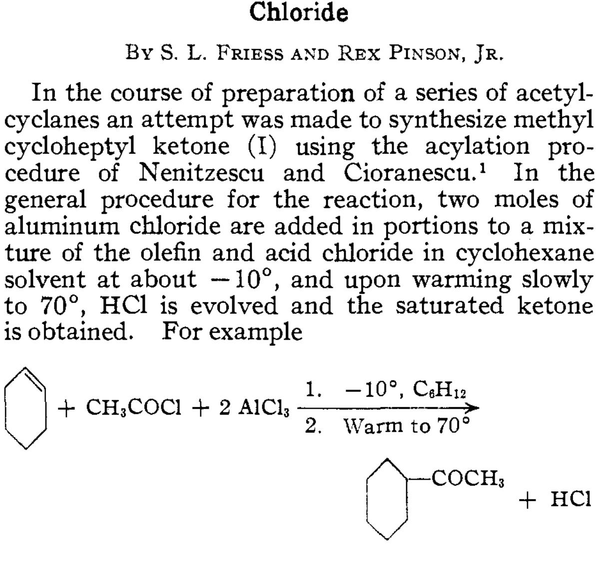
[13] K. Yamasaki, A. Kotera, M. Yokoi and Y. Ueda, *J. Chem. Phys.*, **18**, 1414 (1950).

PHILADELPHIA, PENNA.
RECEIVED FEBRUARY 23, 1951

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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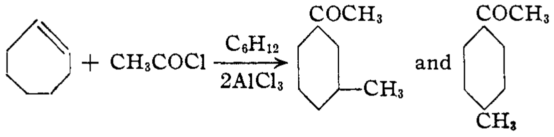
[1] C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69B**, 1820 (1936).

ketone. He pointed out[1] the utility of the reaction with cyclic olefins for producing saturated ketones in which the ring size remains unchanged, in contrast to the reaction of the saturated compound cyclohexane[2,3] with acetyl chloride and aluminum chloride in which ring contraction to a methylcyclopentane derivative occurs.

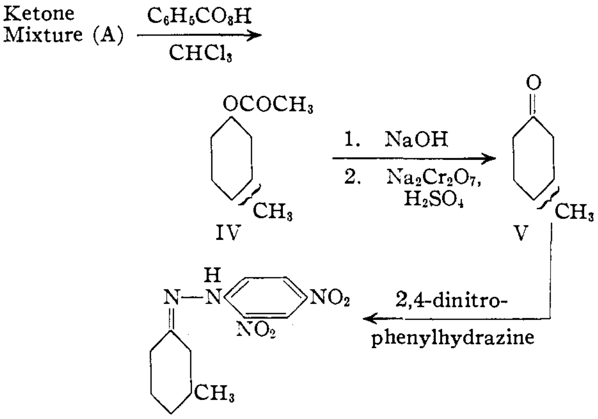
In the present work, it has been observed that the reaction of the olefin cycloheptene does not furnish the normal product (I), but leads to a 40% yield of a mixture (A), which apparently contains methyl 3-methylcyclohexyl ketone (II) and methyl 4-methylcyclohexyl ketone (III).



II III

In preliminary experiments a semicarbazone and a 2,4-dinitrophenylhydrazone prepared from the ketone mixture (A) were found to be different from the corresponding derivatives prepared from an authentic sample of (I).[4] Further, on oxidation of the mixture (A) with sodium hypobromite there was obtained a saturated acid which could be transformed to a solid amide differing from that reported for the amide of cycloheptanecarboxylic acid.

Evidence for the presence of II as a component of the original ketone mixture (A) was obtained by application of the degradation scheme



VI (isolated)

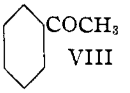
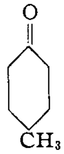
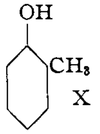
The methyl ketones of the mixture were first converted to the acetates (IV) with perbenzoic acid,[5] followed by saponification and oxidation of the resulting alcohols to the cyclohexanone mixture (V). This sequence of reactions, carried out without purification of intermediates, eliminates the complicating possibilities of stereoisomerism present in (A) and facilitates solution of the simpler problem of the relative positions of the methyl and acetyl groups in the isomeric components of the mixture.

Mixture (V) was converted to its mixture of 2,4-dinitrophenylhydrazones which, after preliminary purification by passage over a column of alumina and repeated fractional crystallization from ethanol gave a small yield of pure (VI). Attempted chromatographic separation[6] of the mixture failed to yield any other pure component.

Evidence for the presence of the 4-methyl isomer in the original mixture (A) was obtained by dehydrogenation with sulfur at the reflux temperature. The ketone product of this reaction was converted to the 2,4-dinitrophenylhydrazone which, upon repeated crystallization from benzene, furnished a small yield of pure *p*-methylacetophenone 2,4-dinitrophenylhydrazone (VII), as shown by mixed melting point behavior with a known sample.

Additional evidence as to the complex nature of (A) was furnished by a study of the apparent C-methyl content of this mixture and of various reference compounds. The method of Barthel and LaForge[7] was employed, with the results shown in Table I.

TABLE I

Compound			
Ketone mixture (A)	 VIII	 IX	 X
0.94	0.83	0.13	0.73

Apparent C-methyl content (moles HOAc/mole of compound)

The data of Table I would appear to indicate that, in addition to the *ca.* 0.8 mole of acetic acid to be obtained from the acetyl group (as in VIII), the presence of an adjacent ring methyl group (X) would lead to an increment of 0.7 mole of acetic acid, whereas a non-adjacent ring methyl group (as in IX) would give in contrast approximately 0.1 mole of acetic acid. The fact that mixture (A) gives slightly more than 0.9 mole of acetic acid therefore points strongly to the absence of any significant amount of a constituent of the mixture possessing a ring methyl group adjacent to the acetyl function. Compounds (IX) and (X) were used as models to evaluate the relative quantities of acetic acid formed from methyl groups at various positions on the ring because of the probability that initial cleavage of the acetyl group in mixture (A) with chromic acid does leave an oxygen function directly on the ring.

It was observed in the course of these C-methyl determinations that methylcyclohexane gives only a trace of acetic acid (*ca.* 0.01 mole), and that to ensure detection of a ring methyl group in this series it is essential that the starting compound possess some polar function to promote solubility in the chromic acid mixture, and prevent escape from the reaction zone because of ready volatility.

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[2] (a) C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **491**, 189 (1931); (b) C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **65**, 1449 (1932).

[3] F. Unger, *ibid.*, **65**, 467 (1932).

[4] Prepared by the method of M. S. Newman and W. T. Booth, THIS JOURNAL, **67**, 154 (1945).

[5] S. L. Friess, *ibid.*, **71**, 14 (1949).

[6] The procedure employed was that of J. D. Roberts and C. Green, *Ind. Eng. Chem., Anal. Ed.*, **18**, 335 (1946).

[7] W. F. Barthel and F. B. LaForge, *ibid.*, **16**, 434 (1944).

Experimental[8]

Acylation of Cycloheptene.—Using 0.5 mole of cycloheptene,[9] 0.5 mole of acetyl chloride, 1.0 mole of granular aluminum chloride, and 100 ml. of cyclohexane as solvent, the acetylation was carried out essentially according to the procedure of Nenitzescu and Cioranescu.[1] In the final distillation of the product (A) there was obtained 28.3 g. (40%, based on olefin) of ketone, b.p. 65–66° at 7 mm., $n^{18}{}_D$ 1.4518.

Product (A) readily formed a semicarbazone, white plates from diluted ethanol, m.p. 169–170°. *Anal.* Calcd. for $C_{10}H_{19}N_3O$: C, 60.89; H, 9.71. Found: C, 61.16; H, 9.53.

A crystalline 2,4-dinitrophenylhydrazone also was formed, m.p. 115–120°.

The oxidation of 5.5 g. of ketone (A) with a sodium hypobromite solution prepared from 24 g. of bromine and 15.2 g. of sodium hydroxide in 140 cc. of water gave a 92% yield of saturated acids, b.p. 121–123° (7 mm.). The acids readily formed an amide (or mixture of amides), white needles from water, m.p. 168–170° (lit. value[10] for the amide of cycloheptanecarboxylic acid, 194–195°).

Preparation of Methyl Cycloheptyl Ketone (I).—An authentic sample of this material was prepared from cycloheptyl bromide in 38% yield by the method of Newman and Booth,[4] and its structure proved by conversion to the acetate ester with perbenzoic acid and saponification to the known product, cycloheptanol.

The ketone was used to prepare a semicarbazone, white plates from 50% ethanol, m.p. 175–176°. *Anal.* Calcd. for $C_{10}H_{19}N_3O$: C, 60.89; H, 9.71. Found: C, 61.01; H, 9.65.

A 2,4-dinitrophenylhydrazone was also prepared, orange-yellow needles from ethanol, m.p. 117–118°. *Anal.* Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29. Found: C, 56.50; H, 6.26.

These derivatives caused depression of the melting points when mixed with the corresponding derivatives of (A).

Reaction of (A) with Perbenzoic Acid.—Using known[5] procedures, a mixture of 7.4 g. (0.053 mole) of (A) and 150 ml. of a chloroform solution containing 0.057 mole of perbenzoic acid was allowed to react at room temperature for three days, and the ester product isolated.

The crude ester was saponified with 25% aqueous sodium hydroxide, the alcohol fraction separated by ether extraction, and the ether solution dried and evaporated. The crude alcohol was oxidized directly.

Oxidation of the Alcohol.—The alcohol obtained above was added in small portions with vigorous shaking to a solution of 8.4 g. of sodium dichromate and 7.0 g. of concentrated sulfuric acid in 42 ml. of water. The temperature rose to about 60°. After all the alcohol had been added, the flask was stoppered and shaken mechanically for two hours. The organic material was removed by ether extraction, and the ether solution washed with 5% sodium hydroxide until the washings were nearly colorless. The ether was evaporated, and the ketones converted directly to a 2,4-dinitrophenylhydrazone mixture, m.p. 110–126°.

Preliminary purification of this derivative was effected by passage through a column of alumina in 1:1 (by volume) benzene-hexane solvent, with a recovery of 95% of crystalline material. Fractional crystallization from 95% ethanol gave a small yield of pure (VI), m.p. and mixed m.p. with an authentic sample, 153–155°. The fractionation process failed to yield any other pure compound. Chromatography on alumina and on silicic acid—Super-Cel[6] also failed to yield any other pure isomer.

Dehydrogenation of (A) with Sulfur.—A mixture of 2.80 g. (0.02 mole) of (A) and 1.92 g. (0.06 g. atom) of powdered sulfur was heated under reflux (190–200°) for 18 hours. Evolution of hydrogen sulfide was noted throughout the interval. The mixture was then steam distilled, and part of the resulting oil was used to prepare a 2,4-dinitrophenylhydrazone, which was recrystallized repeatedly from benzene to a constant melting point; red needles from benzene, m.p. and mixed m.p. with an authentic sample of VII, 253–255°.

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[8] Melting points are corrected; boiling points are uncorrected.

[9] Prepared from cycloheptanol according to the procedure of J. Böeseken and C. J. A. Hanegraaf, *Rec. trav. chim.*, **61**, 69 (1942).

[10] E. Buchner and A. Jacobi, *Ber.*, **31**, 2008 (1898).

Chromones. V. The Preparation of 2-Methyl-7-hydroxychromone and 2-Methyl-5,8-dimethoxy-7-hydroxychromone

BY T. A. GEISSMAN

The preparation of 2-methylchromones from polyhydroxyacetophenones by the reaction of *o*-hydroxyacetophenones with acetic anhydride and sodium acetate[1] is often unsatisfactory because of the formation of 4-methylcoumarin derivatives or of 3-acetyl-2-methyl-chromones which must be deacylated in a separate step. The C-acylation of *o*-hydroxyacetophenone with ethyl acetate and sodium[2] is a reaction which does not readily lend itself to extension to polyhydroxyacetophenones because of the formation of insoluble sodium salts; and the modification of this reaction in which a polyacetoxyacetophenone is used also leads in some cases to 3-acetyl-2-methylchromones.[3] Alternative methods of masking the hydroxyl groups during the condensation of the acetyl group with ethyl acetate include the benzylation and subsequent hydrogenolysis of the benzyloxy groups; but the multiplicity of steps and the over-all losses in yields accompanying such devices caused us to seek a superior method of performing syntheses of 2-methylchromones based upon the resorcinol and substituted resorcinol nucleus.

The successful preparation of 2,6-dihydroxybenzoic acid by a procedure involving the protection of the hydroxyl groups by tetrahydropyranyl ether formation[4] suggested the use of a similar procedure in the present work. The method proved to be an excellent one for the preparation of 2-methyl-7-hydroxychromone (from resacetophenone) and 2-methyl-5,8-dimethoxy-7-hydroxychromone (from 2,4-dihydroxy-3,6-dimethoxyacetophenone). In the case of the former synthesis, intermediates were isolated and characterized in the course of exploratory experiments; in the latter, the several steps were carried out without the isolation of intermediate compounds.

The extension of this reaction to the preparation of 2-methyl-5,7-dihydroxychromone from phloroacetophenone has so far proved to be unsatisfactory.

Experimental

Resacetophenone 4-Tetrahydropyranyl Ether.—To a mixture of 10.0 g. of purified resacetophenone and 25 ml. of redistilled dihydropyran was added 6 drops of concentrated hydrochloric acid. (In later runs *p*-toluenesulfonic acid was used.) The mixture was warmed gently to effect solution of the resacetophenone and allowed to stand overnight in a water-bath at room temperature. Ether and dilute aqueous potassium hydroxide were added and the aqueous layer separated. The ether layer was dried and evaporated and the oily residue converted to 2-methyl-7-hydroxychromone in the manner described below.

The aqueous layer was acidified and extracted with ether. The dried ether solution was allowed to evaporate slowly, and large colorless prisms separated (5.2 g.). Recrystallized from ether-petroleum ether, the compound formed glistening prisms, m.p. 76–78°. The compound gave a wine-red color with methanolic ferric chloride.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.83. Found: C, 66.38; H, 7.23.

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[1] S. v. Kostanecki and A. Rozycki, *Ber.*, **34**, 102 (1901).

[2] G. Wittig, *ibid.*, **57B**, 88 (1924).

[3] T. A. Geissman, unpublished observations; see also W. Baker, *J. Chem. Soc.*, 1381 (1933); 1953 (1934) for related work.

[4] W. E. Parham and E. L. Anderson, THIS JOURNAL, **70**, 4187 (1948).