

The Grignard Reagent Reaches the Freshman

See KING, W. B., AND BEEL, J. A., *J. Chem. Educ.*, **32**, 146-148 (1955).

The reaction of methylmagnesium iodide with ethyl alcohol yields methane as one of the products. From the known molecular weight of alcohol, the weight of alcohol used in the experiment, and the volume of methane produced at a measured temperature and pressure, it is reasonable to conclude that ethyl alcohol has the structure CH_3CHOH .

Questions:

Using the procedure described, suggest a reasonable molecular

structure for other alcohols, such as ethylene glycol, glycerine, propylene glycol, etc. (Determine the molecular weight of the compound selected by measuring its vapor density or by other suitable means.)

Using a suitable modification of the procedure described, suggest a reasonable structure for a different type of compound: a ketone, an amine, an aldehyde, or a carboxylic acid.

Determine the molecular structure of a polyfunctional compound such as urea, morpholine, or aspirin.

Student Experiments on Derivatives of 1,2-diphenylethane

See FIESER, L. F., *J. Chem. Educ.*, **31**, 291-7 (1954).

It is not possible in a brief abstract to convey adequately the depth of interest which this article will engender in any student who is sufficiently conversant with the field of organic chemistry. Unquestionably, this article is outstanding, particularly for the purposes we hope to fulfill in presenting this series to teachers of chemistry. No specific questions will be cited, contrary to our usual custom, since many questions, implicit and explicit, are indicated in the text of the article.

Eight topics are considered, and for each, Dr. Fieser gives his personal comments, in addition to the preparative details:

Reductive Acetylation of Benzil. The two isomers, *cis*- and *trans*-stilbene- α,β -diol diacetate, that are formed are separable. Reductive acetylation of quinones can be catalyzed by several different substances, any of which could be tried by a student. However, though it can be done safely, *the use of perchloric acid is strongly discouraged*—use some of the other catalysts mentioned.

meso-Hydrobenzoin. In this simple preparation from benzil, the student can study the use of various reducing agents such as sodium amalgam, sodium borohydride, etc. With other suitable modifications, benzoin can be used as the starting material. It is perhaps possible to isolate *dl*-hydrobenzoin from the mother liquor and effect resolution of this *dl*-diol, ultimately, by mechanical separation of the enantiomeric crystals similar to the pattern of Pasteur's classical method.

trans-Stilbene. A special method is described, adapted to a 1-2 gram scale. It would be interesting to compare this method with other preparative procedures for the same compound.

meso-Stilbene Dibromide. Using pyridinium bromide perbromide, *trans*-stilbene is converted to the *meso*-dibromide.

Other brominating agents could be used. The properties of this product should be compared with those of the *dl* isomer, discussed below.

Diphenylacetylene. The rate of dehydrobromination depends upon the temperature of refluxing. This effect can be studied or other techniques used to obtain the unsaturated product.

α -Phenylcinnamic Acid. Both the *cis* and *trans* isomers are formed in this synthesis. They can be separated by their difference in solubility in acidic media. This difference is correlated with the sharp difference in pK_a values of each isomer, and would constitute an interesting study in itself.

cis-Stilbene. This compound is prepared from the *cis* isomer of the cinnamic acid derivative, above, by decarboxylation. The rate of decarboxylation depends upon the temperature. The product is not easily purified and characterized as to purity. Purification and characterization constitute an interesting challenge. Decarboxylating agents, other than copper chromite in quinoline, may be used.

dl-Stilbene Dibromide. Bromination of *cis*-stilbene yields *dl*-stilbene dibromide. If crude *cis* isomer is used, some *meso* dibromide is formed from the *trans* isomer that is present in small amount in the crude material.

Since *dl*-stilbene dibromide can be prepared readily from crude *cis*-stilbene, debromination of this compound should occur by *trans* elimination and yield pure *cis*-stilbene. In the discussion following this observation, the existence of a catalytic effect by zinc bromide upon *cis-trans* isomerization of stilbene and other related phenomena raise many more questions, each sufficiently interesting to stimulate many other investigations.

Sequence of Synthesis in the General Organic Laboratory

See LANGE, E. F., TERANISHI, R., AND CHRISTENSEN, B. E., *J. Chem. Educ.*, **32**, 40-41 (1955).

p-xylene is oxidized to terephthalic acid; part of this acid is converted to acid chloride and the methyl ester formed in a following step. The remainder of the terephthalic acid is nitrated, and the nitroterephthalic acid reduced to the amine derivative. From this, 4-quinazalone-7-carboxylic acid is prepared.

Questions:

Compare the ease of oxidation of *p*-xylene to terephthalic acid with the oxidation of toluene to benzoic acid.

Following the same general outline, what other compounds can you prepare, starting with a compound homologous or isomeric with *p*-xylene?

What other compounds can you prepare from 4-quinazalone-7-carboxylic acid?

Dimethylterephthalate is useful in the synthesis of polymers; prepare this compound and determine the conditions necessary for polymerization.