epimerization of the original ribofuranose **6** during the acidic fusion reaction since the identity and purity of **6** were established prior to the fusion reaction. The fusion reaction has been applied to the preparation of many purine and pyrimidine nucleosides[23,24]—mostly nucleosides from 1,2,3,5-tetra-*O*-acetyl-D-ribofuranose—and epimerization has not been observed heretofore. Whether the unique structure of this sugar is responsible for epimerization in this case is not known,[25] but the most logical mechanism by which it might occur would be migration of the 1-acetoxy group of β-**6** to C-2 *via* an ortho ester–ion intermediate. In any event, the occurrence of epimerization in this widely used reaction makes conclusive proof of the structure of nucleosides prepared in this manner vital.

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[25] Preparation of the glycosyl chloride from **6** by treatment with ethereal HCl at 0° in the usual manner was accompanied by epimerization detected by its pmr spectrum. Reaction of this chloride with 2,6-dichloropurine gave a mixture of β-*ribo*-**9** and α-*arabino*-**9** along with lesser amounts of the respective anomers.

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Activated Metals. I. Preparation of Highly Reactive Magnesium Metal

Sir:

We would like to report a new method for preparing magnesium metal in a very reactive state. Previous to our studies, there were three modifications of the general procedure for the direct synthesis of difficultly formed Grignard reagents from the reaction of magnesium metal and an organic halide: (1) use of higher reaction temperatures, (2) use of a more strongly coordinating solvent,[1-5] and (3) activation of the magnesium metal.[6-10] The third method consists of activation of the magnesium by reduction of the size of the metal particle[9] or by a chemical reaction. The Gilman catalyst,[6] which involves the addition of iodine to activate the magnesium, is representative of this technique. Ethylene bromide or ethyl bromide has been employed in catalytic amounts to activate the magnesium surface and in molar quantities as an entrainer.[7] Use of certain transition metal halides has proven them to be useful catalysts.[8] Recently, Ashby combined the three techniques to prepare some alkylmagnesium fluorides.[10]

Our new process produces magnesium in a finely divided state and free of any metal oxides. The reactivity of this metal is vastly superior to that of any of the methods described above. For example, we have prepared phenylmagnesium bromide from phenyl bromide and our activated magnesium in THF at −78°. In only 30 min over a 60% yield was realized. The per cent yield of the Grignard reagent was based on the amount of benzoic acid produced upon treatment with carbon dioxide. Treatment of chlorobenzene with normal magnesium at room temperature for 90 min gave no phenylmagnesium chloride. In contrast, treatment of chlorobenzene with our activated magnesium at room temperature for 90 min yielded 62% of phenylmagnesium chloride. Reaction with phenyl bromide at room temperature is very exothermic and very rapid. Within 2–3 min yields of over 65% phenylmagnesium bromide were realized. Further evidence of the high reactivity of the metal comes from the reaction of fluorobenzene with the activated metal. Until this report, all efforts to prepare phenylmagnesium fluoride from fluorobenzene and magnesium had failed.[10] These attempts included use of all the modifications listed at the beginning of this paper and in some cases involved reflux times of several days. Refluxing fluorobenzene and our activated metal in diglyme for only 1 hr yielded over 5% benzoic acid after treatment with carbon dioxide.[11]

The general process for generating the finely divided metal involves the reduction of anhydrous magnesium chloride or anhydrous magnesium bromide[12] in an inert ethereal solvent under an inert atmosphere. The reduction can most conveniently be carried out by using an alkali metal and an ethereal solvent whose boiling point exceeds the melting point of the alkali metal. The metal salt to be reduced should be at least partially soluble in the ethereal solvent chosen. Solvent combinations that we have found useful are potassium–THF and diglyme–sodium.[13] The reaction time for reduction varies from 1 to 2 hr for the THF–K–MgX_2 combination to 5–6 hr for the diglyme–Na–MgX_2 combination. The reduction yields a fine black powder of magnesium metal which can be immediately used to prepare the Grignard reagent. In most cases, the Grignard reagents were prepared by simply adding the alkyl or aryl halide directly to the suspension of powdered magnesium metal. No attempt was made to remove the sodium or potassium salts formed in the reductions. We have removed the original solvent from the powdered metal in some cases either by vacuum or decanting. This metal powder gave similar results to that described above. Any problem with unreacted alkali metals can be avoided by starting with an excess of magnesium halide.

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[11] Use of transition metal halides as catalysts, higher reflux temperatures, and longer reaction times are being currently investigated.

[12] The chloride has the advantage of being commercially available whereas the magnesium bromide must be prepared from magnesium and ethylene bromide.

[13] At this point, we have not tried dimethoxyethane but we are certain it will work also. Dioxane did not work.

The basic procedure seems to be quite general and any reducing agent (chemical or electrical) with a higher potential than the metal salt will work. We have also prepared a number of other activated metals by this procedure and find that they too have unusual reactivity. We will be reporting on these metals and further reactions of the activated magnesium in the near future.

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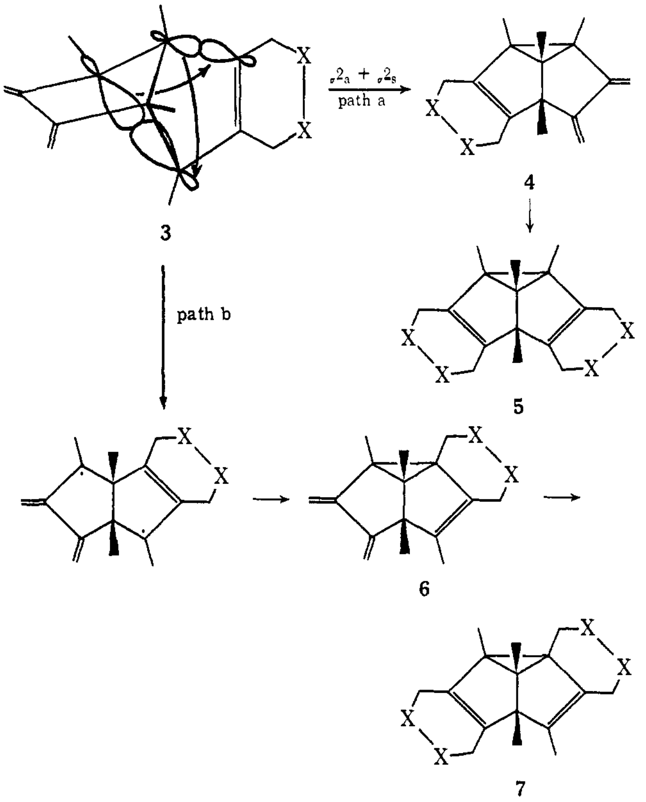
The Mechanism of Rearrangement of Molecules Containing Cyclobutane Rings 1,3 Bridged by Ethylene

Sir:

Although kinetic[1] and stereochemical[2] studies of the rearrangement of cyclobutanes 1,3 bridged by ethylene have been interpreted in terms of energetically proximate concerted ${}_{\sigma}2_{a} + {}_{\pi}2_{s}$[3] and biradical[4] pathways, the extraordinary facility of the rearrangement of tricyclo[3.3.0.0^{2,6}]octadiene (**1**) to semibullvalene[5,6] has prompted the suggestion[7,8] that this and similar[7] molecules may rearrange by a symmetry-allowed[3] but rarely observed[9,10] ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ mechanism. In this communication we present experimental evidence that rules out a ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ pathway in the extremely rapid rearrangement of an ethylene-bridged cyclobutane but which is wholly consistent with the biradical[4] mechanism originally proposed for the rearrangement of **1**.[5,6]

Recently, we reported that 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**2**) undergoes Diels–Alder reaction with 2 mol of tetracyanoethylene (TCNE) in refluxing THF to give a bisadduct for which we suggested the structure **7a**.[11] The fact that when only 1 equiv of TCNE is used a mixture consisting of equal amounts of bisadduct and starting material **2** is obtained indicates that the second Diels–Alder reaction must be much faster than the first. The lack of Diels–Alder reactivity shown by molecules containing a cyclobutane ring 1,3 bridged by butadiene[12] suggests that the initial monoadduct **3a** rearranges more rapidly than it reacts with another mole of TCNE and that the rearrangement product then undergoes the rapid Diels–Alder reaction expected of a normal diene. This reaction scheme is illustrated below for both a ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ (path a) and biradical[4] (path b) mechanism for the rearrangement of **3a**.



a, X–X = (NC)$_2$C–C(CN)$_2$ b, X–X = NCON(Ph)CON

The bisadducts **5a** and **7a** expected from the two different mechanisms for the rearrangement differ in that the former possesses a plane of symmetry while the latter has an effective C_2 axis on the nmr time scale.[13] Thus, only two types of methyl groups should appear in the nmr spectrum of **7a**, while three different methyl resonances might be anticipated in the nmr of **5a**. We previously reported that the methyl groups in the nmr spectrum of the bisadduct appear as two sharp singlets at 100 MHz in acetone-d_6.[11] We have now obtained 220-MHz spectra of this compound in both acetone-d_6 and pyridine-d_5.[14] Despite the fact that the broad singlet from four of the methylene protons[11] is now resolved into an AB quartet, the methyl resonances remain sharp singlets.

Although the nmr spectra provide evidence against the structure **5a**, they cannot be considered as unequivocal proof of the correctness of structure **7a** for the product. Moreover, the nmr data from further bisadducts of **2** can increase the likelihood that **4** is the correct structure but never demand it. Experimentally, **2** proves so reluctant to undergo Diels–Alder cycloaddition that, despite our attempts with such reactive dienophiles as

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[12] We find that whereas the reaction of 1,2-dimethylenecyclobutane with tetracyanoethylene in THF is instantaneous at room temperature, that of 2 requires several hours at reflux for completion.

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