cyclobutyl ethyl ketone (ir 1710, 1247, 1132, and 970 cm^{-1}, identical with product from Jones oxidation of 1-cyclobutyl-propanol).

Propylidenecyclopentane oxide gave a single product in 84% yield: nmr δ 5.4 (s, 1), 4.0 (t, 1, J = 6 Hz, CH–OH), 2.9 (d, 1, J = 3 Hz, OH, shifts with formic acid), 2.5–1.2 (m, 8), and 0.85 ppm (t, 3, J = 6.5 Hz, CH$_3$); ir 3320, 1090, and 900 cm^{-1}.

Propylidenecyclohexane oxide after 49 hr gave 9% unreacted epoxide and a 69% yield of two products. **3c** (95%): nmr δ 5.35 (m, 2), 2.3 (s, 1, shifts with formic acid, OH), 1.7 (d, 3, J = 5 Hz, CH$_3$), and 1.55 ppm (broad singlet, 10); ir 3370 and 970 cm^{-1}. **2c** (5%): nmr δ 5.47 (t, 1, J = 2.5 Hz, C=CH), 3.7 (t, 1, J = 6.5 Hz, CH–OH), 2.5 (s, 1, OH), 2.2–1.2 (m, 10), and 0.8 ppm (t, 3, J = 7 Hz, CH$_3$); ir 3330, 1003, 960, and 917 cm^{-1}.

Propylidenecycloheptane oxide was consumed within 5 hr, giving 76% of two volatile products. **2d** (98%): nmr δ 6.2 (t, 1, J = 7 Hz, C=CH), 4.1 (t, 1, J = 7 Hz, CH–OH), 2.7–1.3 (m, 13), and 0.9 ppm (t, 3, J = 8 Hz, CH$_3$); ir 3320, 1020, and 850 cm^{-1}. The minor product, **3d** (2%), was identified by catalytic reduction to 1-propylcycloheptanol which was the major product from LiAlH$_4$ reduction of the epoxide.

Propylidenecyclooctane oxide after 2 hr gave 74% of a single product, **2e**: nmr δ 5.75 (t, 1, J = 8 Hz, C=CH), 4.0 (t, 1, J = 7 Hz, CH–OH), 2.2 (m, 4), 1.6 (broad singlet, 9), and 0.9 ppm (t, 3, J = 8 Hz, CH$_3$); ir 3350, 1100, and 850 cm^{-1}.

Propylidenecyclododecane oxide was completely rearranged in 22 hr, yielding 66% of a product mixture. The major component (84%) was shown to be **2f**: nmr δ 6.0 (t, 1, J = 8.5 Hz, C=CH), 4.9 (t, 1, J = 7.5 Hz, CH–OH), 2.6–2.0 (m, 4), 2.0–1.2 (m, 19), and 1.0 ppm (t, 3, J = 8 Hz, CH$_3$); ir 3370, 1090, 1010, and 970 cm^{-1}. Two lesser components, 12 and 4%, were not elucidated.

Ethylidenecyclopentane oxide after 1.5 hr gave 82% of two products. The major product (70%) was **8a**: nmr δ 6.2 (s, 1), 4.85 (quartet, 1, J = 7.5 Hz, CH–OH), 3.5 (s, 1), 2.9–1.8 (m, 6), and 1.4 ppm (d, 3, J = 7 Hz, CH$_3$); ir 3340, 1160, and 1075 cm^{-1}. The remainder (30%) was **9a**: nmr δ 6.1–4.8 (ABC pattern, 3) and 2.0–1.2 ppm (m, 8), OH peak variable; ir 3360, 3080, 990 (doublet), and 920 cm^{-1}.

Ethylidenecyclohexane oxide rearranged to a single product in 66% yield, **9b**: nmr δ 7.0–5.4 (ABC pattern, 3), 2.2 (s, 1, OH),

and 1.7 ppm (broad singlet, 10); ir 3370, 3070, 1265, 995, 965, 925, and 910 cm^{-1}.

Ethylidenecycloheptane oxide gave a 74% yield of two allylic alcohols. The minor alcohol (38%) was **8c**: nmr δ 5.85 (t, 1, J = 6.5 Hz, HC=C), 4.16 (quartet, 1, J = 6.5 Hz, CH–OH), 2.8 (s, 1, OH), 2.4–1.9 (m, 4), 1.9–1.3 (m, 6), and 1.16 ppm (d, 3, J = 7 Hz, CH$_3$); ir 3340, 1080, 1063, 986, and 848 cm^{-1}. The major product **9c** comprised 62% of the mixture: nmr δ 6.4–4.9 (ABC pattern, 3), 2.3 (s, 1, –OH), and 1.62 (broad singlet, 12); ir 3370, 1035, 1000, and 920 cm^{-1}.

Ethylidenecyclooctane oxide also led to a mixture of two alcohols in 73% overall yield. **8d** (66%): nmr δ 5.42 (t, 1, J = 8 Hz, HC=C), 4.05 (quartet, 1, J = 6 Hz, CH–OH), 3.2 (s, 1, OH), 2.1 (broad singlet, 4), 1.46 (s, 8), and 1.17 ppm (d, 3, J = 6.5 Hz, CH$_3$); ir 3330, 1160, 1100, 1062, and 848 cm^{-1}. **9d** (34%): nmr δ 6.0–4.6 (ABC pattern, 3) and 1.55 ppm (broad singlet, 15, includes OH); ir 3375, 1160, 995, 972, and 919 cm^{-1}.

Isobutylidenecyclohexane oxide, after 72 hr reflux, was up to 76% unreacted. The sole product was **12**: nmr δ 5.4 (s, 1, HC=C), 4.6 (s, 1, OH), 3.36 (d, 1, J = 7.5 Hz, CH–OH), 2.3–1.2 (m, 9), and 0.83 ppm (two overlapping doublets, 6); ir 3400, 1140, 1014, and 915 cm^{-1}.

Registry No.—Propylidenecyclobutane, 28253-07-8; propylidenecyclopentane, 4810-12-2; propylidenecyclohexane, 2129-93-3; propylidenecycloheptane, 17257-34-0; propylidenecyclooctane, 28256-52-2; propylidenecyclododecane, 28256-53-3; ethylidenecyclopentane, 2146-37-4; ethylidenecycloheptane, 10494-87-8; ethylidenecyclooctane, 19780-51-9; isobutylidenecyclohexane, 28256-56-6; **1a**, 28256-57-7; **1b**, 28256-58-8; **1c**, 28256-59-9; **1d**, 28256-60-2; **1e**, 28256-61-3; **1f**, 28256-62-4; **7a**, 28256-63-5; **7b**, 17328-74-4; **7c**, 28256-65-7; **7d**, 28256-66-8; **11**, 28256-67-9.

On the Rigidity to Carbanion Inversion of Four-, Five-, and Six-Membered Cyclic Organomagnesium Compounds

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Several 1,1-dimethylcycloalkylmagnesium halides were synthesized and their nmr spectra obtained as a function of temperature. Each reagent gave rise to an equal doublet for the methyl resonance. The nmr spectra were independent of the temperature, and it is concluded that carbanion inversion is slow on the nmr time scale up to 175°. The various effects responsible for this result are discussed in terms of what is known about the mechanism of inversion in primary Grignard reagents. It is concluded that carbon bridging in Grignard dimers is not favored when the bridging group is cycloalkyl.

Inversion rates of carbon bonded to metal in primary organometallic compounds of lithium, magnesium, aluminum, and zinc have been reported.[1-5] However, so far there has been relatively little work on inversion in secondary systems. Letsinger found 2-octyllithium inverted slowly at low temperatures.[6] Jensen and Nakamaye determined the endo/exo ratio for 2-norbornylmagnesium bromide.[7] This reagent also inverted slowly.[7]

While our work on inversion in primary organometallic systems was proceeding, we initiated some experiments on secondary reagents. Meanwhile, Whitesides and Roberts[2] discussed the behavior of the nmr spectra of 3,3-dimethylcyclobutylmagnesium bromide and 2,4-dimethylpentylmagnesium bromide-3 and concluded carbanion inversion to be slow on the nmr time scale.[2] Also, Glaze and Selman have reported 4-*tert*-butylcyclohexyllithium to be configurationally stable.[8]

The approach we have chosen consists of synthesizing various 1,1-dimethylcycloalkylmagnesium halides, I, and obtaining their nmr spectra as a function of tem-

(1) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 2854 (1965).

(2) G. M. Whitesides and J. D. Roberts, *ibid.*, **87**, 4878 (1965).

(3) G. Fraenkel and D. T. Dix, *ibid.*, **88**, 979 (1966).

(4) M. Witanowski and J. D. Roberts, *ibid.*, **88**, 737 (1966).

(5) G. Fraenkel, D. T. Dix, and M. J. Carlson, *Tetrahedron Lett.*, 579 (1968).

(6) R. L. Letsinger, *J. Amer. Chem. Soc.*, **72**, 4842 (1950).

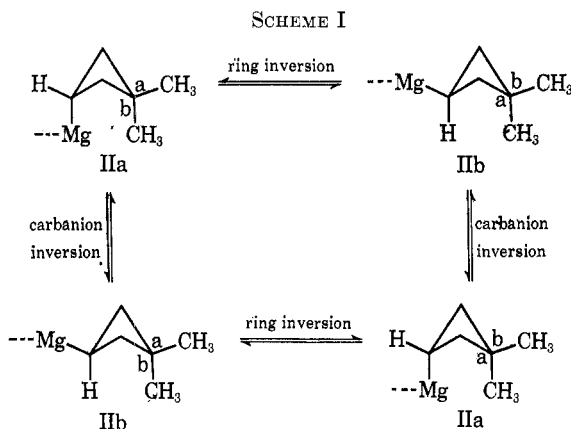(7) F. R. Jensen and K. L. Nakamay, *ibid.*, **88**, 3437 (1966).

(8) W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, **11**, 3 (1968).

perature. From the results together with a considera-
tion of what is known about ring inversion in these
systems it should be possible to obtain at least qualita-
tive information about carbanion inversion rates.

I
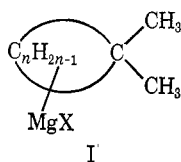
First, it is assumed that, although organomagnesium
compounds exist in solution as mixtures of aggregates,
carbon–magnesium bond exchange in ethers is still
fast enough at $-70°$ to average any shifts among
species.[9,10] However, in the presence of organomag-
nesium alkoxides and certain diamines, carbon–mag-
nesium bond exchange rates have been measured with
the nmr line-shape method.[9]

By analogy to what is known about cyclobutanes,
3,3-dimethylcyclobutylmagnesium bromide should exist
in two conformations.[11–14] The methyl groups in each
should give rise to a doublet. Fast ring inversion
and slow carbanion inversion should average the shifts
between the conformers to a single doublet, while
if both processes are fast all the methyl resonances
will be averaged to a single line. It is already known
that inversion in cyclobutanes is fast on the nmr
time scale down to $-100°$.[15,16] Hence, it should be
possible to estimate the rate of inversion from the
methyl proton nmr line shape[17,18] (see Scheme I).

SCHEME I

The arguments for the other cyclic Grignard reagents
follow those for the cyclobutyl reagent. In the case
of cyclohexanes, shifts among conformers are usually

averaged out by fast chair to chair inversion by $60°$.[19]
Finally, for 2,2-dimethylcyclopentylmagnesium bro-
mide, we need not consider ring inversion and the
pseudorotation discussed by Brutcher and Baur[20] is
probably too fast to be detected by nmr spectroscopy.

We proceed below to describe the syntheses of the
Grignard reagents and their precursors. It will be
shown that inversion in cyclic organomagnesium com-
pounds is slow compared to the primary reagents.

Results and Discussion

3,3-Dimethylcyclobutanecarboxylic acid[21,22] was con-
verted to 3,3-dimethylbromocyclobutane (III), by
means of the Hunsdiecker reaction,[2] run in pentane.

Kishner's method,[22] the action of fuming HBr on
cyclobutyldimethylcarbinol followed by work-up with
base, afforded 2,2-dimethylcyclopentyl bromide (IV),
together with two olefins which were identified to be
1,2-dimethylcyclopentene and isopropylidenecyclobu-
tane.

The preparation of 2,2-dimethylcyclohexyl bromide
(V) from cyclopentyldimethylcarbinol and fuming
HBr[23] gave also two olefins identified to be isopropyli-
denecyclopentane and 1-isopropylcyclopentene.

When cyclopentyldimethylcarbinol was treated with
60% sulfuric acid at $80°$ for 4 hr, the products con-
sisted of 1-isopropylcyclopentene (47%), isopropyli-
denecyclopentane (50%), and traces of isopropenyl-
cyclopentane. The absence of ring-expanded products
in this experiment is consistent with the finding of
Johnson and Owyang that 2,2-dimethylcyclohexanol
subjected to formolysis conditions slowly contracts to
various five-membered ring compounds[24] and that the
formation of cation VI is reversible.

VI
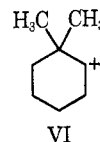
The synthesis of 4,4-dimethylcyclohexyl bromide
(VII) was accomplished by halo decarboxylation of
4,4-dimethylcyclohexanecarboxylic acid (see Experi-
mental Section for precursors).

Finally, 3,3-dimethylcyclohexyl bromide (VIII) was
synthesized by a modification of Doering's procedure,[25]
reacting the corresponding alcohol with hydrogen bro-
mide.

The cyclic halides III, IV, V, VII, and VIII reacted
with magnesium in ether, THF, and dimethoxymethane
to give mainly coupling products and only low yields
of the corresponding Grignard reagents IX–XIII.
However, in diglyme at $60°$ these halides were smoothly

(9) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

(10) The possibility of degenerate shifts among species will not alter the interpretations.

(11) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(12) G. W. Rathjens, Jr., and W. D. Gwinn, *J. Amer. Chem. Soc.*, **75**, 5629 (1953).

(13) G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *ibid.*, **75**, 711 (1961).

(14) A. Almennigen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(15) R. P. Bauman and B. J. Balkin, *J. Chem. Phys.*, **45**, 496 (1966).

(16) S. Meiboom, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 26T.

(17) H. S. Gutowsky, D. M. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(18) In the event of accidental degeneracy of all the methyl shifts, no conclusions can be drawn.

(19) (a) M. Friebolin, W. Faisst, M. G. Schmid, and S. Kabuss, *Tetrahedron Lett.*, 1317 (1966); W. Reusch and D. F. Anderson, *ibid.*, 253 (1966); R. J. Abraham and D. B. MacDonald, *Chem. Commun.*, 188 (1966); also reviewed in J. D. Roberts, *Chem. Brit.*, 529 (1966). (b) Exceptions to this generalization include 3,3-difluoromethylcyclohexane, 4,4-difluoromethylcyclohexane, and 4,4-difluorobutylcyclohexane: S. L. Spassov, P. L. Griffith, E. S. Glazer, N. Nagarajan, and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 88 (1967).

(20) F. V. Brutcher and W. Baur, Jr., *Science*, **132**, 1489 (1960).

(21) A. Campbell and H. N. Ryden, *J. Chem. Soc.*, 3002 (1953).

(22) N. Kishner, *Chem. Zentralbl.*, I, 543 (1911); *ibid.*, II, 1859 (1908).

(23) S. S. Nametkin and M. A. Volodina, *Zh. Obshch. Khim.*, **21**, 331 (1951).

(24) W. S. Johnson and R. Owyang, *J. Amer. Chem. Soc.*, **86**, 5595 (1964).

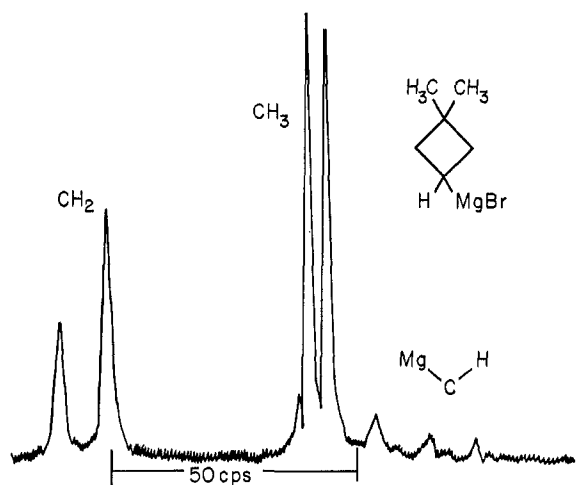(25) W. v. E. Doering and F. M. Beringer, *ibid.*, **71**, 2221 (1949).

Figure 1.—Nmr spectrum (60 MHz) of 3,3-dimethylcyclobutyl-magnesium bromide, 1.4 M in diglyme, 40°.

converted to Grignard reagents in nearly quantitative yields. Attempts were made to convert these halides to organolithium compounds. The only bromide which underwent this conversion in high yield was III. The nmr spectra of the hydrolysates of these organometallic reagents showed only absorption belonging to the corresponding hydrocarbon.

The nmr spectra of reagents IX–XIII are illustrated in Figures 1–4. Chemical shift assignments are labeled on the spectra. Methyl resonances of contained impurities are listed as RH or RBr.

Only in the case of 3,3-dimethylcyclobutylmagnesium bromide is it possible to resolve all the different hydrogens. Each reagent gives a single multiplet for the methine hydrogen, H–C–Mg. These shifts are listed in Table I. For all the reagents with the ex-

TABLE I

H–C–Mg SHIFT IN x,x-DIMETHYLCYCLOALKYLMAGNESIUM
BROMIDES, 1 M IN DIGLYME

Reagent	Ring size	x	τ
IX	4	3	9.16
X	5	2	10.60
XI	6	2	10.30
XIII	6	3	10.05
XII	6	4	10.30

ception of 3,3-dimethylcyclobutylmagnesium bromide (Figure 1), the methylene hydrogens belong to strongly coupled systems and give rise to complex multiplets. Finally, each reagent in diglyme gives rise to two lines for the methyl hydrogens (Figure 3). The nmr spectrum of 3,3-dimethylcyclobutyllithium is shown in Figure 2b. This spectrum clearly shows magnetically nonequivalent methyls, also. Other details concerning these spectra will be discussed below.[26]

The nmr spectra of the Grignard reagents were obtained from 40 to 175°. Aside from changes in resolution which attend changes in viscosity, the line positions and intensities were independent of the temperature. However, at the higher temperatures,
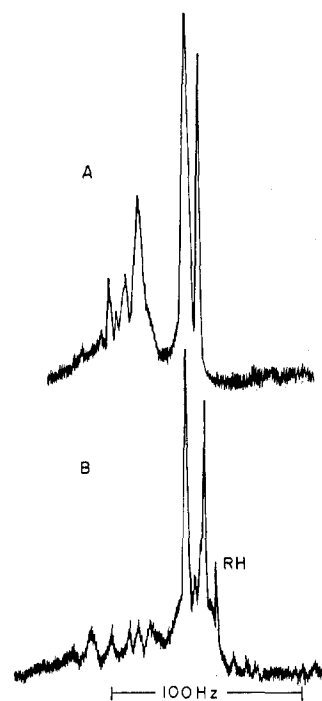
Figure 2.—Nmr spectra (60 MHz), 40°, of (a) 3,3-dimethyl-cyclohexylmagnesium bromide, 1.4 M in diglyme, and (b) 3,3-dimethylcyclobutyllithium, 1.3 M in benzene.

around 170°, each sample underwent slow irreversible changes as a result of which the spectrum of the Grignard reagent was eventually replaced by that of its hydrolysate. This behavior is illustrated for 3,3-dimethylcyclohexylmagnesium bromide in Figure 4. Evidently at the higher temperatures the reagents abstract protons from the solvent. Due to viscosity broadening it was not possible to obtain useful nmr data from these solutions below 10°. The sample of 3,3-dimethyl-cyclobutyllithium decomposed above 60° and was not further investigated.

On the basis of the discussion in the introduction, the conclusions for the four- and five-membered ring reagents are quite clear. Down to −100° cyclobutanes invert at rates which are fast on the nmr time scale. The simplicity of the H–C–Br resonance in III, as well as the H–C–Mg resonances in its Grignard reagent IX, indicates ring flipping to be fast in the cyclobutyl compounds. The methyl resonance of 3,3-dimethyl-cyclobutylmagnesium bromide consists of two lines. Therefore, this reagent undergoes slow carbanion inversion up to 175°. Since pseudorotation in the five-membered reagent X is probably fast, the persistence of a methyl doublet up to 175° indicates slow carbanion inversion in this case, also. This same conclusion applies to the cyclohexylmagnesium bromides; carbanion inversion is slow up to 175° and ring inversion is fast above 40°. The latter is evident also from the simplicity of the H–C–Mg resonances of these Grignard reagents and is also found for their precursors.[27]

Jensen and Nakamaye have resolved shifts among the two chair conformers of cyclohexylmagnesium reagents[28] at low temperatures. The observation of two

(26) In one case, 3,3-dimethylcyclohexylmagnesium bromide in dimethoxymethane, there is fine structure in the methyl resonance indicative of slowly interconverting species. Above 50° the lines broaden slightly; however, the shifts remained constant.

(27) In contrast to this result we find that the carbinyl resonance of 3,3-dimethylcyclohexyl bromide is quite complicated and has the appearance of the resonance in a substituted cyclohexane undergoing slow ring inversion.

(28) F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.,* **90,** 3248 (1968).
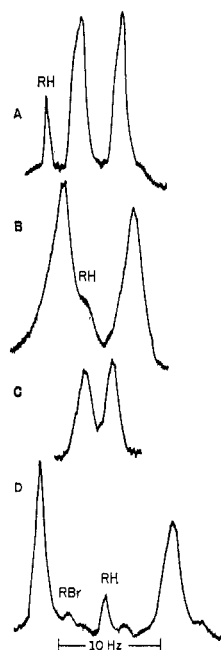
Figure 3.—Methyl group nmr from (a) 4,4-dimethylcyclohexyl-magnesium bromide, (b) 3,3-dimethylcyclohexylmagnesium bromide, (c) 2,2-dimethylcyclohexylmagnesium bromide, and (d) 2,2-dimethylcyclopentymagnesium bromide. All reagents are 1.4 M in diglyme, 40°.

resonances for these materials at −85° implies both ring and carbanion inversion to be slow at 'his temperature. Either one or both of these processes could be responsible for averaging the two H–C–Mg resonances at higher temperatures. These authors assign the axial and equatorial H–C–Mg hydrogen shifts to be τ 10.25 and 9.76.[28] If these values apply to our solutions of substituted cyclohexylmagnesium reagents in diglyme, it would appear that the 2,2-dimethyl- and 4,4-dimethylcyclohexylmagnesium bromides exist mainly in the conformations with the C–Mg bond equatorial.

In view of the above discussion it would appear that the persistence of doublets for the methyl resonances of 2,2- and 4,4-dimethylcyclohexylmagnesium bromide indicates these reagents to be inverting slowly on the nmr scale up to 175°.

In summary, we find here that carbanion inversion in four-, five-, and six-membered cycloalkylorganomagnesium compounds is slow in the nmr time scale up to 175°. This situation applies also to cyclopropyl-magnesium compounds. Walborsky has found these to be configurationally stable for long periods of time.[29]

The maximum reciprocal mean lifetime between inversions at 175° for the reagents studied here is 1 sec⁻¹, while the extrapolated value for 2-methylbutyl-magnesium bromide is 1.2 × 10⁻⁵ sec⁻¹. In spite of the qualitative nature of the results, it is worthwhile to consider why carbanion inversion in the cyclic organomagnesium compounds should be so much slower than in the primary reagents.

The most convincing rationale for the data presented here comes from a consideration of the results from kinetic studies on inversion in primary systems. The available data indicate that inversion takes place in
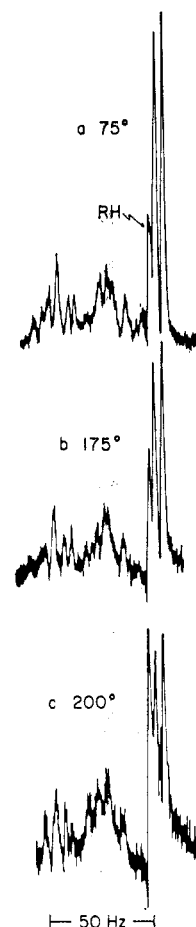

Figure 4.—Nmr spectra showing effect of heating 4,4-dimethyl-cyclohexylmagnesium bromide, 1.4 M in diglyme (a) after 10 min at 75°, (b) after 15 min at 175°, and (c) after 30 min at 200°.

dimers of 2-methylbutylmagnesium halides and that the transition state for inversion involves carbon bridging.[30] At the present time, it is not known whether carbon bridging is involved in Grignard dimers in the ground state. So far, there is no firm evidence for any of the structures which have been proposed for Grignard dimers.[31] If alkyl bridging takes place in the transition state for Grignard inversion, then bridging would be most likely for primary compared to secondary and tertiary groups, respectively. Such is the case among bridged organoaluminum compounds.[32]

The principle conclusion from this work is that carbanion inversion in cyclic organomagnesium bromides is slow on the nmr time scale up to 175°, and this effect is ascribed to the inability of secondary groups to bridge between magnesium centers.

Experimental Section

Physical Constants.—All boiling points were those obtained during distillation and are uncorrected. All melting points were determined using a capillary apparatus or a Fisher-Johns apparatus and are uncorrected.

Analyses.—Elemental microanalyses of synthesized compounds were carried out by the microanalytical laboratories of Dr. A. Bernhardt, Mühlheim, Germany, or Galbraith Analytical Laboratories.

Spectrometric Methods.—Nuclear magnetic resonance spectra

(29) H. M. Walborsky and F. J. Impasato, *J. Amer. Chem. Soc.*, **81**, 5835 (1959).

(30) G. Fraenkel, C. Cottrell, and D. T. Dix, *ibid.*, submitted for publication.

(31) E. C. Ashby, *Quart. Rev., Chem. Soc.*, **21**, 259 (1967).

(32) E. G. Hoffmann, *Justus Liebigs Ann. Chem.*, **629**, 104 (1960).

were obtained on a Varian Model A-60 spectrometer. Infrared absorption spectra were obtained with a Perkin-Elmer Model 137 sodium chloride spectrometer. Vapor phase chromatographic work was undertaken with an Aerograph Hy-Fi Model 600 and an Aerograph "Autoprep" Model A-700. All analyses determined by vpc have been corrected for the weight:area factor utilizing an internal standard, except where otherwise designated. All vpc analyses were obtained with a 30% silicon gum rubber SE-30 on 45-60 Chromosorb W or 20% FFAP on 60-80 Chromosorb W.

3,3-Dimethylcyclobutyl Bromide (III).—A suspension of 3,3-dimethylcyclobutanecarboxylic acid (40 g, 0.312 mol) in 600 ml of distilled water was neutralized with 13 ml of 30% ammonium hydroxide. A solution of silver nitrate (53.2 g, 0.312 mol) in 200 ml of distilled water was added dropwise to the stirred solution of the acid. An additional 100 ml of water was added and the white precipitate was filtered, washed with water and then methanol, and dried in an oven at 50-60°. For the next step, the dried silver salt was powdered and sieved into a crystal dish. The silver salt was now dried in a vacuum oven at 80° for 60 hr. The yield consisted of 70 g (90.4%) of silver 3,3-dimethylcyclobutane-carboxylate.

The finely powdered silver salt (70 g, 0.298 mol) was placed in a 1-l. three-necked flask equipped with a dropping funnel, reflux condenser, and mechanical stirrer. All this equipment had been thoroughly dried in an oven at 100°. To the salt was added 360 ml of olefin-free dry pentane. While stirring, bromine (47.7 g, 0.298 mol), dried over phosphorus pentoxide, was slowly added through the dropping funnel over a period of 45 min. At first cooling was necessary, as the exothermic reaction was quite vigorous. When all the bromine had been added, the mixture was heated under reflux for 1 hr. It was then filtered and the silver bromide was washed on the filter with 100 ml of pentane. The filtrate was washed once with 200 ml of a 10% sodium bisulfite solution and then with distilled water and dried over magnesium sulfate. Evaporation of the solvent and distillation of the residue afforded 26.5 g (54.7%) of 3,3-dimethylcyclobutyl bromide as a colorless oil, bp 45.5-46.5° (32 mm) (lit.[2] bp 132°).

The purity of the compound was confirmed by vpc. The infrared spectrum (NaCl, neat) showed strong bands (cm⁻¹) at 2900, 1440, 1405, 1340, 1360, 1230, 990, and 788. The nmr spectrum (benzene, TMS internal standard) showed resonance at τ 5.80 (quintet, methine), 7.77 (multiplet), 8.99 (singlet, methyl), and 9.19 (singlet, methyl).

Anal. Calcd for $C_6H_{11}Br$: C, 44.18; H, 6.80; Br, 49.02. Found: C, 44.15; H, 6.76; Br, 49.09.

The Hunsdiecker reaction with 3,3-dimethylcyclobutane-*1-d*-carboxylic acid-*d* resulted in the formation of 3,3-dimethylcyclobutyl bromide-*1-d*.

2,2-Dimethylcyclopentyl Bromide (IV).—In a 250-ml two-necked flask equipped with a thermometer and a cooling tube was placed cyclobutyldimethylcarbinol (53.5 g, 0.468 mol). Approximately 50 ml of fuming hydrobromic acid was slowly added with cooling by means of an ice bath. The mixture was then heated in an oil bath with magnetic stirring at 100° for 2 hr. Much HBr was lost at this time. The resulting olive green solution was poured in a separatory funnel and washed a few times with distilled water. The lower layer of crude bromide was transferred to an erlenmeyer flask and heated with a solution of 20 g of potassium hydroxide in 50 ml of water at 100° for 2 hr. The bromide layer was separated, poured into a 100-ml flask, and, after addition of water, steam distilled. The bromide was dissolved in ether, washed with water, and finally dried over magnesium sulfate. The ether was then removed by distillation and the residual liquid distilled under reduced pressure to give 16 g of a fraction of isomeric olefins and 30.7 g (36.2%) of 2,2-dimethylcyclopentyl bromide, bp 55-56° (15 mm), as a colorless oil (lit.[22] bp 167°, partial dec). The purity of the bromide was confirmed by vpc. The infrared spectrum (NaCl, neat) showed strong bands at 2870, 1435, 1365, 1345, 1245, 1175, 838 and 804 cm⁻¹. The nmr spectrum (CCl₄, TMS internal standard) showed resonance at τ 6.13 (X portion of ABX, methine, $J_{AX} + J_{BX} - 15$ cps), 7.55-8.60 (multiplet, methylene), and 8.96 (singlet, methyl).

Anal. Calcd for $C_7H_{13}Br$: C, 47.48; H, 7.39; Br, 45.13. Found: C, 47.31; H, 7.57; Br, 45.12.

Further evidence for the correct structure of the bromide came from the hydrocarbon obtained by hydrolysis of the corresponding Grignard reagent. The nmr spectrum of 1,1-dimethylcyclopentane (diglyme) showed at τ 8.15-8.85 (multiplet, methylene) and 8.98 (singlet, methyl). The peak areas were in ratio 4:3.

The isomeric olefins formed as side products from the preparation of the bromide were separated by vpc. Two components were obtained in the ratio of 4.5 to 95.5. The spectral properties of the lower boiling component established its structure to be isopropylidenecyclobutane: ir (NaCl, neat) max 2990, 2890, 2805, 1645, 1365, 1325, 1077, 1015, 915, and 797 cm⁻¹; nmr (CCl₄) τ 4.78 (center of complex multiplet, terminal vinyl protons), 7.38-8.15 (multiplet, methylene, methine), and 8.39 (singlet, methyl).

The second component was identified as 1,2-dimethylcyclopentene-1 by comparison of its nmr spectrum and retention time to those of an authentic sample: nmr (CCl₄) τ 7.51-8.35 (multiplet, methylene) and 8.44 (singlet, methyl).

2,2-Dimethylcyclohexyl Bromide (V).—In a 500-ml two-necked flask equipped with a thermometer and cooling tube were placed cyclopentyldimethylcarbinol (110 g, 0.858 mol) and 100 ml of fuming hydrobromic acid. The mixture was then heated in an oil bath with stirring at 100° for 3 hr. The heavier brown bromide layer was separated from the water. It was transferred to a 500-ml erlenmeyer flask and heated with stirring with a solution of 40 g of potassium hydroxide in 100 ml of water at 100° for 2 hr. The heavier crude bromide layer was separated, poured into a 1-l. flask, and steam distilled. The distilled product was dissolved in ether, washed with water, and dried over magnesium sulfate. The ether was removed and the residue distilled under reduced pressure to give a fraction of isomeric olefins, bp 40-60° (23 mm), and 99.4 g (60.6%) of colorless 2,2-dimethylcyclohexyl bromide, bp 85-85.5° (23 mm) [lit.[24] bp 85.5° (23 mm)]. The purity of the bromide was confirmed by vpc. The infrared spectrum (NaCl, neat) showed strong bands at 2870, 2885, 1448, 1430, 1367, 1348, 1200, 960, 854, 715, and 676 cm⁻¹. The nmr spectrum (CCl₄, TMS internal standard) showed resonance at τ 5.95 (ABX, methine, $J_{AX} + J_{BX} = 15.0$ cps), 7.58-8.79 (multiplet, methylene), and 8.92 (singlet, methyl).

Anal. Calcd for $C_8H_{15}Br$: C, 50.28; H, 7.91; Br, 41.81. Found: C, 50.35; H, 7.87; Br, 41.78.

The structure and identity of 2,2-dimethylcyclohexyl bromide was further proved by its chemistry.

A Grignard solution prepared in diglyme was hydrolyzed and the resulting hydrocarbon was compared in its spectral properties and retention time to a commercial sample of 1,1-dimethylcyclohexane. Their properties were the same: ir (NaCl, neat) max 2880, 2800, 1430, 1360, 1345, 1165, 957, and 846 cm⁻¹; nmr (CCl₄) τ 8.23-8.87 (multiplet, methylene) and 9.08 (singlet, methyl).

The Grignard reagent of the above bromide in ether was oxidized with molecular oxygen and the resulting alcohol compared to an authentic sample of 2,2-dimethylcyclohexanol. Both compounds showed the same spectral properties and vpc retention times. Treatment of the alcohol with phenyl isocyanate resulted in a phenylurethane which melted at 84.5-85° (lit.[33] mp 84-85°). The infrared spectrum (NaCl, neat) of the alcohol was characterized by a hydroxyl band at 330 cm⁻¹.

Side Products from Cyclopentyldimethylcarbinol-HBr Reaction.—The olefin fraction consisted of two components which were separated by vpc (XIV and XV). Samples (1 g) of these olefins were ozonized in methylene chloride at −78° for about 1 hr. The blue ozonide solution was poured into a flask containing 50 ml of water. The methylene chloride was removed on a steam bath. In both cases the water residue contained oils. The ozonized product of the lower boiling olefin XIV was soluble in a 5% solution of sodium bicarbonate, indicating an acid, whereas the product from olefin XV was insoluble. The alkaline solution from olefin XIV was acidified, extracted in ether, and gave a very high boiling oil. With semicarbazide hydrochloride it gave a semicarbazone, mp 183-185°. The melting point was close to that reported for the semicarbazone of 6-methyl-5-oxy-heptanecarboxylic acid, mp 182.5-183.5°.[23]

Infrared and nuclear magnetic resonance spectra further proved the identity of olefin XIV as 1-isopropylcyclopentene-1: ir (NaCl, neat) max 3030, 2960, 1645, 1358, 1375, 1305, 1290, 1067, 1033, 948, and 807 cm⁻¹; nmr (CCl₄) τ 4.75 (singlet, vinyl), 7.50-8.52 (multiplet, methine, methylene), and 9.00 (doublet, methyl, $J = 6.0$ cps).

The ozonized olefin XV was neutral and gave, after treatment with semicarbazide hydrochloride, a semicarbazone, mp 207-209°, very close to the reported melting point for the semicarbazone of

(33) H. Meerwein, *Justus Liebigs Ann. Chem.*, **405**, 142 (1914).

cyclopentanone,[34] mp 209–210°. The infrared and nuclear magnetic resonance spectra identified olefin XV as isopropylidinecyclopentane: ir (NaCl, neat) max 2910, 2820, 1645 (w), 1435, 1420, 1360, 1095, and 945 cm⁻¹; the nmr spectrum (CCl₄) showed no vinyl protons.

Reaction of Dimethylcyclopentylcarbinol with Sulfuric Acid.— When the dimethylcyclopentylcarbinol was heated with 60% sulfuric acid at 80° for 4 hr, it resulted in the formation of three compounds. All three decolorized bromine indicating alkenes. These were XIV (47%), isopropenylcyclopentane (2%) [XVI, 888 cm⁻¹ (C=CH₂)], and XV (51%) [bp 136° (lit.[23] bp 136–137°)].

Preparation of 3,3-Dimethylcyclohexyl Bromide (VIII).—The procedure used was a modification of that of Doering.[26] In a 100-ml three-necked flask equipped with a mechanical stirrer, reflux condenser, and insert tube was placed 3,3-dimethylcyclohexanol (32 g, 0.25 mol). A stream of hydrogen bromide was passed through the alcohol for 30 min at 5°, for 15 min at 100°, and for 2 hr at 130°. The reaction product was first washed with concentrated sulfuric acid with an equal amount of 50% methanol, with ammonium hydroxide until basic, and finally again with 50% methanol. Distillation of the dried product gave 31 g (64.8%) of colorless 3,3-dimethylcyclohexyl bromide, bp 63–63.5° (8 mm) [lit.[26] bp 80–82° (5 mm)].

The purity of the bromide was confirmed by vpc. The infrared spectrum (NaCl, neat) showed strong bands at 2880, 1445, 1373, 1350, 1330, 1312, 1285, 1250, 1235, 1205, 1170, 1130, 1042, 966, 945, 921, 840, 831, 715, and 695 cm⁻¹. The nmr spectrum (CCl₄, TMS internal standard) showed resonance at τ 5.64–6.30 (complex, multiplet, methine), 7.55–8.86 (complex, multiplet, methylene), 9.06 (singlet, methyl), and 9.09 (singlet, methyl).

Anal. Calcd for C₈H₁₅Br: C, 50.28; H, 7.91; Br, 41.81. Found: C, 50.22; H, 7.91; Br, 41.91.

Treatment of the Grignard reagent from VIII (0.02 mol) with 1-naphthyl isocyanate (1.69 g, 0.01 mol) gave, after recrystallization from methanol, a derivative with mp 201–202.5°, very close to the reported melting point of N-1-naphthyl-3,3-dimethylcyclohexanecarboxamide (lit.[25] bp 204–204.5°).

1,5-Dibromo-3,3-dimethylpentane.—Diethyl β,β-dimethylglutyrate was prepared by Perkin's procedure.[35] The ester was reduced to 3,3-dimethyl-1,5-pentanediol with lithium aluminum hydride.[36] To 3,3-dimethyl-1,5-pentanediol (71.5 g, 0.542 mol) was added, slowly, phosphorus tribromide (149 g, 0.55 mol) with stirring. The reaction mixture was heated at 90° for 12 hr. The ether layer was washed with sodium carbonate, dried over magnesium sulfate, and filtered. After evaporation of the ether, the residue was distilled under vacuum to give 116 g (83.2%) of colorless 1,5-dibromo-3,3-dimethylpentane: bp 86–86.5° (2 mm) [lit.[37] bp 80–81° (1.3 mm)]; ir (NaCl, neat) νmax 2940, 1468, 1450, 1385, 1365, 1330, 1235, and 755 cm⁻¹.

4,4-Dimethylcyclohexane-1,1-dicarboxylic Acid.—The acid was prepared modifying the procedure of Otto.[37] In a 5-l. three-necked flask equipped with a mechanical stirrer, reflux condenser with a drying tube, and a dropping funnel was placed 2000 ml of absolute ethanol. The ethanol was slowly reacted with sodium (20.7 g, 0.96 g-atom) added over a period of 2 hr. Diethyl malonate (71 g, 0.45 mol) was added to the above solution followed by 1,5-dibromo-3,3-dimethylpentane (116 g, 0.448 mol). The reaction mixture was refluxed with stirring for 4 days. A solution of 100 g of sodium hydroxide in 500 ml of aqueous ethanol (50%) was then added and the refluxing continued for 10 hr. Ethanol was removed by steam distillation and the residual solution was acidified with hydrochloric acid, extracted with ether, and washed with distilled water. After the ethereal extract was dried over magnesium sulfate, the ether was evaporated and white crystals of 4,4-dimethylcyclohexane-1,1-dicarboxylic acid, mp 190–190.5° (reported[37] mp 190–192°), were obtained, yield 71 g (79.2%).

4,4-Dimethylcyclohexanecarboxylic Acid.—4,4-Dimethylcyclohexane-1,1-dicarboxylic acid (70.7 g, 0.353 mol) was heated with 0.3 g of powdered Pyrex glass in a 1-l. flask equipped with a reflux condenser carrying a thermometer. Evolution of carbon dioxide commenced soon after all the diacid had melted. The temperature was held for about 2 hr at 220°. Upon cooling,

the residue solidified to shiny white needles. Recrystallization from ethanol–water gave 53.4 (95.8%) of 4,4-dimethylcyclohexanecarboxylic acid, mp 45–46° (reported[37] mp 45–47°).

4,4-Dimethylcyclohexyl Bromide (VII).—The acid just described was converted to the bromide by the Hunsdiecker reaction of the silver salt, in a procedure similar to that described above. Thus, 53.4 g of 4,4-dimethylcyclohexanecarboxylic acid gave with silver nitrate (58.3 g, 0.343 mol) and 82 g (91.2%) of dry silver salt.

The dry silver 4,4-dimethylcyclohexanecarboxylate (81.5 g, 0.31 mol) was allowed to react with bromine (49.5 g, 0.31 mol) in 500 ml of dry pentane. Work-up of the product in the usual manner resulted in 26.5 g (40.5%) of colorless VII, bp 57–58° (5 mm). The purity of the bromide was confirmed by vpc. The infrared spectrum (NaCl, neat) showed strong bands at 2850, 1455, 1440, 1325, 1305, 1285, 1250, 1205, 1172, 1135, 982, 973, 935, 842, 714, 699, and 686 cm⁻¹. The nmr spectrum (CCl₄, TMS internal standard) showed resonance at τ 5.87 (center of symmetrical multiplet, methine), 7.72–8.89 (multiplet, methylene), 9.04 (singlet, methyl), and 9.10 (singlet, methyl).

Anal. Calcd for C₈H₁₅Br: C, 50.28; H, 7.91; Br, 41.81. Found: C, 50.05; H, 7.84; Br, 42.05.

Preparation of the Organometallic Compounds. Solvents.— The solvents used for the preparation of organometallic compounds were distilled directly into the reaction vessel from a flask containing drying reagent. Diethyl ether was distilled from commercial methylmagnesium bromide. Dimethoxymethane, n-pentane, and benzene were distilled from lithium aluminum hydride. Diglyme was distilled twice from lithium aluminum hydride and then from methylmagnesium iodide under reduced pressure (50 mm).

Metals.—Lithium metal dispersed in wax and containing 1% of sodium was used for the preparation of the lithium compounds. The wax was removed just before reaction by washing the dispersion several times with dry solvent. Triply sublimed magnesium milled into fine shavings was used for the preparation of the Grignard compounds. The shavings were washed with dry ether, dried in a stream of helium, and stored in a desiccator.

Apparatus.—Hypodermic syringes were used for the addition of the bromides and the transfer of the organometallic compounds. The syringes were equipped with a stopcock and 6- or 8-in. 18-gauge needles.

Vacuum vials, fitted with a 1-mm straight bore stopcock and a 12/30 male joint, were used sometimes for storing or purification of organometallic reagents. All the above mentioned equipment was cleaned and dried in a current of argon prior to its use.

Instrumentation.—All nmr spectra of organometallic compounds were obtained with a Varian A-60 high resolution nmr spectrometer.

Procedures for the Preparation of Organometallic Compounds. Grignard Reagents (General).—The reaction vessel consisted of a 2.6-cm o.d. test tube equipped with a 24/40 outer joint at the open end and an 8-mm-o.d. side arm with straight bore Teflon stopcock. The apparatus was flamed out in a current of argon and loaded with a Teflon stirring bar together with the required amount of magnesium. It was then quickly attached to the receiving end of the still used to purify solvent. The solvent was then distilled over in two 20-ml portions. Each was removed by a hypodermic syringe. Finally, a 10-ml portion was distilled over, stirring was begun, and a few drops of the bromide were added to the reaction vessel through the Teflon stopcock. Sometimes reaction set in within a few minutes, but in some instances, heating or addition of 1–3 drops of 1,2-dibromoethane was necessary. The remaining bromide was then added at the rate of about 1 mmol/min, and the mixture heated afterward for 2 hr to complete reaction. Stirring was then discontinued, and the magnesium was allowed to settle. Aliquots were taken for nmr and base analysis. Most of the Grignard reagents were prepared in diglyme at 50°. Specific procedures follow.

3,3-Dimethylcyclobutylmagnesium Bromide—Into the helium-flushed reaction vial containing magnesium (0.965 g, 0.036 g-atom) was distilled 10 ml of dry diglyme. Stirring was started after the flask was immersed in an oil bath and heated to 50°. 3,3-Dimethylcyclobutyl bromide (29.3 g, 0.018 mol) was added slowly by means of a hypodermic syringe through the Teflon stopcock. The reaction mixture became cloudy after the first few drops, indicating initiation of the reaction. The rest of the bromide was added and stirring continued for 2 hr at 50°. A considerable amount of white solid precipitated after the solution had come to room temperature. One sample of the clear solution

(34) O. Aschau, *Ber.,* **45**, 1606 (1912).

(35) W. H. Perkin, *J. Chem. Soc.,* 1457 (1896).

(36) A. T. Blomquist and E. S. Wheeler, *J. Amer. Chem. Soc.,* **77**, 6307 (1955).

(37) B. Otto, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1963.

was withdrawn from the reaction vessel and injected through a syringe cap into a dry nmr tube. The latter was cooled with liquid nitrogen and sealed with a hot flame. Another sample was titrated with 0.1 N hydrochloric acid (methyl orange as indicator), indicating a 1.5 M solution (95%). The nmr spectrum of the hydrolysate showed absorption only for 1,1-dimethylcyclobutane (τ 8.90).

Registry No.—3,3-Dimethylcyclobutyl bromide, 4237-75-6; 2,2-dimethylcyclopentyl bromide, 22228-38-2; isopropylidenecyclobutane, 1528-22-9; 2,2-dimethylcyclohexyl bromide, 28268-91-9; 1-isopropylcyclopentene, 1462-07-3; isopropylidinecyclopentane, 765-83-3; 3,3-dimethylcyclohexyl bromide, 25090-98-6;

4,4-dimethylcyclohexyl bromide, 25090-97-5; 3,3-dimethylcyclobutylmagnesium bromide, 4237-72-3; 3,3-dimethylcyclohexylmagnesium bromide, 28268-97-5; 4,4-dimethylcyclohexylmagnesium bromide, 28268-98-6; 2,2-dimethylcyclohexylmagnesium bromide, 28268-99-7; 2,2-dimethylcyclopentylmagnesium bromide, 28269-00-3.

Organophosphorus Compounds. XII.[1a] ¹H and ³¹P Nuclear Magnetic Resonance Spectroscopic Studies of the Protonation and Cleavage of Trialkyl (Aryl) Phosphates and Phosphites, Dialkyl Phosphonates, and Phosphorus Oxy Acids in FSO₃H and FSO₃H–SbF₅ Solution

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Protonation and cleavage of phosphoric acid, phosphonic acid, phosphinic acid, trialkyl (aryl) phosphates, trialkyl (aryl) phosphites, and dialkyl phosphonates were studied in fluorosulfuric acid and fluorosulfuric acid–antimony pentafluoride solution. ¹H and ³¹P nmr spectra of the phosphonium ions [including the hydroxyphosphonium ions H$_n$P(OH)$_{4-n}$⁺, n = 0–2], as well as those of the precursors, were obtained generally at −60°. Tetravalent phosphoryl compounds were protonated on the phosphoryl oxygen atom; tervalent compounds were protonated at the phosphorus atom. The nmr data showed that in the protonated intermediates there was a substantial amount of back-donation of the oxygen nonbonded electron pairs to the empty phosphorus d orbital. By raising the temperature, several of the protonated compounds were subject to decomposition reactions, including carbon–oxygen bond cleavage and fluorination.

The chemical behavior of phosphates and phosphites under acidic conditions has long been a subject of interest to many investigators.[2] The acidic solvolyses[3] and the dealkylation by hydrogen halides[4] of phosphate triesters have been examined in detail. Arbuzov's classic paper[5] is the foundation of our understanding of the reactions of phosphite triesters with hydrogen halides.[4] Not only have interactions of phosphite triesters with other strong acids been studied,[6] but protonation by a variety of donors has also been invoked.[2] Dialkyl phosphonates are similarly dealkylated by hydrogen halides;[4] they also participate in other acid-catalyzed reactions.[7]

The chemistry of the parent monophosphorus oxy acids with regard to other acids is of interest as a model for the reactions of the organophosphorus compounds. The electrochemistry[8] and self-condensation[9] of ortho-

phosphoric acid have been explained by autoprotolysis: $2H_3PO_4 \rightleftharpoons P(OH)_4^+ + H_2PO_4^-$. Oxygen isotope exchange between phosphoric acid and water is acid catalyzed.[10] The acid-catalyzed equilibration of the tautomeric forms of phosphonic acid[11] and phosphinic acid has been considered to be important in the many acid-catalyzed oxidation and isotope exchange experiments which have been conducted with these acids.[2]

However, fewer efforts have been made to obtain protonated phosphates and phosphites (the intermediates assumed to arise from the interactions with acids) sufficiently stable for direct observation. There are varying views on the stability of the complexes that phosphoric acid forms with hydrochloric acid and perchloric acid,[12] where phosphoric acid is thought to be a proton acceptor. Sulfuric acid is viewed as a proton donor to phosphoric acid,[12e,13] and ³¹P nuclear magnetic resonance chemical shifts of phosphates in sulfuric acid

(1) (a) Part XI: G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **34**, 1832 (1969). (b) National Institutes of Health Predoctoral Research Fellow, 1968-1970. (c) Taken in part from the Ph.D. Dissertation of C. W. McFarland, Case Western Reserve University, 1971.

(2) The reactions with acids of the types of phosphorus compounds with which this paper is concerned, with emphasis on the involvement of protonated intermediates, have been thoroughly reviewed: C. W. McFarland, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971.

(3) Recent reviews of acidic solvolyses can be found in (a) E. Cherbuliez, *Chimia*, **15**, 327 (1961); (b) C. A. Bunton, *Accounts Chem. Res.*, **3**, 257 (1970).

(4) W. Gerrard, *J. Chem. Soc.*, 218, 1464 (1940), and subsequent papers.

(5) A. E. Arbuzov, *Zh. Russ. Fiz.-Khim. Obshchest.*, **38**, 687 (1906); *J. Chem. Soc., London, Abstr.*, **92i**, 275 (1907).

(6) (a) A. E. Arbuzov, *Zh. Russ. Fiz.-Khim. Obshchest., Chast Khim.*, **46**, 291 (1914); *Chem. Abstr.*, **8**, 2551 (1914), and later papers; (b) A. N. Pudovik and V. K. Krupnov, *J. Gen. Chem. USSR*, **38**, 196, 306 (1968).

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