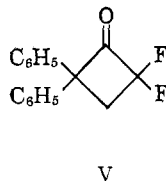IV   V

V, which were included for control purposes since the systems most likely are planar, exhibited essentially constant values of δ over the 225° range, whereas compounds IIIb–e showed variations from 102 (IIId) to 277 c.p.s. (IIIe).

TABLE I

CONFORMATIONAL PROPERTIES OF SUBSTITUTED CYCLOBUTANES

	IIIb	IIIc	IIId	IIIe	IV	V
ΔF, cal./mole	900 ± 100	1100	700	400	...	...
p, 31°	0.816 ± 0.025	0.859	0.761	0.659	...	...
J, c.p.s.	193ᵃ	183	187	198	192	249
δ, −85°,ᵇ c.p.s.	1093	635	425	413	470	37
δ, −30°, c.p.s.	1039	609	393	302	468	39
δ, 31°, c.p.s.	979ᶜ	569	358	225	472	42
δ, 85°, c.p.s.	933	543	336	175	472	43
δ, 140°, c.p.s.	908	522	323	136	470	45
δ_{II}, c.p.s.	1185 ± 10	670	510	965	...	...
δ_I, c.p.s.	60 ± 50	−50	−110	−1220	...	...

ᵃ The coupling constants and chemical shifts are accurate to ±1 c.p.s. except where noted. ᵇ Although the temperatures were measured accurately, these figures are only approximate. ᶜ Data for IIIa and IIIb are nearly identical. This corroborates the assumption regarding the similarity of the geometry of these compounds.

The free-energy difference between the two conformations and the populations of each are related to the equilibrium constant K for eq. 1

$$K = p/(1 - p) = e^{-\Delta F/RT} \tag{2}$$

where p is the mole fraction of II. At fast exchange, the measured chemical shift δ is the weighted average of the chemical shifts of the individual conformers, δ_{II} and δ_I.

$$\delta = p\delta_{II} + (1 - p)\delta_I \tag{3}$$

Thus, one obtains the linear equation

$$\delta = \delta_I + p(\delta_{II} - \delta_I) \tag{4}$$

where $p = e^{-\Delta F/RT}/(1 + e^{-\Delta F/RT})$. The best linear plots of eq. 4 (δ vs. p from assumed values of ΔF) readily give values of ΔF, p, δ_{II}, and δ_I (Table I). The results qualitatively fulfill expectations. The bulky phenyl group (IIIb and IIIc) prefers to reside in the equatorial position. Replacement of the phenyl group by chlorine (IIId) raises the population of the axial conformer and lowers the free energy difference between the conformers. When there are two substituents (IIIe) the populations are more nearly equal, and the free-energy difference is considerably smaller. The fact that δ_I for all monosubstituted compounds is in the vicinity of 0 c.p.s., whereas δ_{II} varies greatly with the substituent, indicates that conformation I may be nearly planar for IIIb–IIId. Further evidence on this point will be forthcoming.

In summary, the n.m.r. method determines the presence or absence of planarity and the dipole-moment method determines the magnitude of puckering. Investigations are in progress to combine these methods in order to predict the angle of puckering in all cases studied.

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CONTRIBUTION No. 3009   JOSEPH B. LAMBERT[11]
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY   JOHN D. ROBERTS
PASADENA, CALIFORNIA

Microcatalytic Tracer Studies of the Isomerization of Cyclopropane over Silica–Alumina Catalysts

Sir:

According to a widely accepted notion stemming from Roberts,[1] the cyclopropane ring is opened when a catalyst proton attaches itself to a ring carbon forming an n-propyl carbonium ion. The isomerization is completed by loss of another proton to the catalyst surface. Indeed, if protons are involved, it is difficult to visualize an alternative reaction path if the tetrahedral valence requirement of carbon is not to be exceeded. The results presented herein do not support this notion; instead, they are indicative of a bimolecular process. These experiments incidentally demonstrate a new technique for the study of catalytic mechanisms.

If an exhaustively deuterated catalyst is contacted with cyclopropane, the Roberts mechanism[1] predicts that the initial product propylene should contain nearly one deuterium atom per molecule. The microcatalytic technique affords an advantageous way of testing this point. Successive small slugs of reactant may be passed quickly over the catalyst and onto a chromatographic column where propylene is separated from unisomerized cyclopropane. These fractions are collected separately and analyzed by mass spectrometry. A plot of the deuterium concentration in the product propylene vs. slug number should extrapolate to unity at zero slug number. Two situations can be visualized depending upon the ratio of cyclopropane molecules, n_g per slug, to the available D⁺, n_a. If $n_a \gg n_g$, the plot should have a gentle slope; if $n_a \ll n_g$, the slope should be high, the fraction of deuterated propylene falling nearly to zero with the first several slugs. No deuterium is expected in the unisomerized cyclopropane and any that appears lowers the amount of propylene that might have formed by reaction with a catalyst deuteron.

A typical set of results selected from one of over a dozen such experiments is shown in Fig. 1. In this
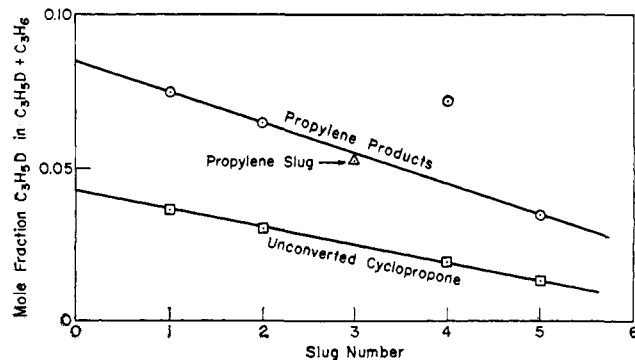

Fig. 1.—Analysis of products from a microcatalytic tracer experiment.

experiment, 8.3 cc. (NTP) slugs of cyclopropane was passed at 148° over 1.657 g. of Houdry M-46 catalyst (265 m.²/g.) which had been repeatedly exchanged with excess D_2O before a final overnight evacuation at 550°. Multiply deuterated products were not obtained.

The behavior was not as predicted by the Roberts mechanism. Less than 10% of the initial propylene can be accounted for on this basis. Moreover, nearly as much deuterium appeared in the unconverted cyclopropane as in the propylene. When propylene was passed instead of cyclopropane (third slug) it became deuterated to the same extent as that produced in the ring-opening reaction. Evidently, most of the deuterium

(1) R. M. Roberts, J. Phys. Chem., 63, 1400 (1959).

found in the products enters *via* a side reaction not involved in the isomerization. These results do not exclude the possibility that the isomerization takes place by repeated use of a very small number of Bronsted sites, but an upper limit is defined for the number of these, *i.e.*, not more than several per cent of n_g. By generous estimate, this amounts to $n_a = 0.01$ mmole ($n_g = 0.37$ mmole) or $1 \times 10^{12}/\text{cm.}^2$, a value much lower than current estimates of Bronsted[2] or Lewis[3] acidity. Taking $1.5 \times 10^{14}/\text{cm.}^2$ as the surface concentration of OD groups,[4] the total available deuterium was 1.1 mmole. The cumulative deuterium removed from the catalyst was 0.06 mmole while 0.54 mmole of olefin was produced.

In these experiments, a portion of the first slug (and smaller amounts of succeeding ones) was retained on the catalyst and lost from the mass balance. This was particularly noticeable in experiments where larger amounts of catalyst and smaller slug size were employed, here, nearly all of the first slug and large portions of the second were so consumed. In all cases, however, about the same amount of hydrocarbon disappeared from 5 slugs, *viz.*, $\sim 10^{13}/\text{cm.}^2$. In order to test for the possible interaction of such residues, propylene-d_6 was circulated over a deuterated catalyst at 155° for 20 min. During this treatment, the gas phase was monitored by a mass spectrometer and C_5 and C_6 species were observed; it was estimated that $8 \times 10^{12}/\text{cm.}^2$ propylene molecules had been irreversibly adsorbed. Slugs of cyclopropane were then passed using helium carrying gas. The results obtained did not differ substantially from those shown in Fig. 1. Similarly, when the conversion level was raised to over 90% by increasing the temperature from 148 to 160°, the extent of deuteration was not greatly different; in fact, the cyclopropane-d_1 fraction from this experiment exceeded that of propylene-d_1. These observations strengthen the view that isomerization and hydrogen exchange do not involve a common mechanism, although they may involve a common intermediate.

Some further insight into the processes taking place was gained from an experiment in which slugs of an equimolar mixture of cyclopropane and cyclopropane-d_6 were passed over the same catalyst at the same temperature. Extensive mixing occurred and multiply deuterated products were formed. The distribution of these did not appear to change with slug number. The mole percentages of the possible cyclopropane products from the third slug were: d_0, d_1–d_6 = 31, 14, 7, 3, 7, 14, and 24. The corresponding values for the propylenes were: 13, 18, 11, 10, 15, 20, and 13. These results are consistent with the recent finding of Larson and Hall[5] that a bimolecular complex is operative in the exchange of isobutane hydrogen with deuterated cracking catalysts.

The distribution of products is not the equilibrium distribution; it is inverted and suggests that the exchange process is stepwise. No large isotope effects were found. The ratio of reacting cyclopropane-d_6 to cyclopropane was about 1.05. This would seem to rule out any concerted mechanism or any step involving the transfer of hydrogen as rate determining.

This work is continuing and is being extended to studies of the double bond isomerization of butene-1 and the dealkylation of cumene. A full report of this work will be made at a later date.

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(3) H. P. Leftin and W. K. Hall, *Actes Congr. Intern. Catalyse, 2e, Paris, 1960*, 1, 1353 (1961).

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(5) J. G. Larson and W. K. Hall, *J. Am. Chem. Soc.*, **85**, 3570 (1963).

MELLON INSTITUTE　　　　　　　　　　　W. KEITH HALL
PITTSBURGH, PENNSYLVANIA　　　　　　JOHN G. LARSON
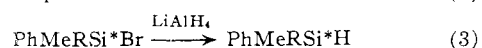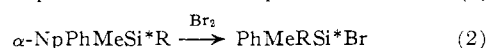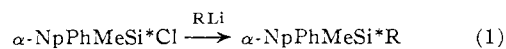　　　　　　　　　　　　　　　　　　　　H. R. GERBERICH

Stereochemistry of Asymmetric Silicon: Synthesis, Stereochemistry, and Absolute Configurations of New Optically Active Organosilicon Systems

Sir:

Studies of optically active triorganomonofunctional silicon systems have previously been limited to compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi–. The finding of many stereospecific reactions of compounds containing this group and elucidation of their stereochemistry[1-4] have made it important to determine whether parallel behavior would obtain for other optically active organosilicon systems.

We wish to report: (a) a synthetic route (which is widely applicable) for conversion of compounds containing the α-NpPhMeSi– group to optically active compounds containing the groups PhMeRSi– in which R is neopentyl, benzhydryl, or ethyl, (b) a high degree of stereospecificity for reactions of the new systems which thus far parallel those of the original system, (c) assignment of absolute configuration to compounds containing the new systems.

The synthetic route to new systems uses optically active α-NpPhMeSi*Cl and an organolithium compound, RLi, for conversion to α-NpPhMeSi*R,[5] and cleavage of the α-naphthyl group with bromine, as α-bromonaphthalene to give PhMeRSi*Br,[6] which is then converted to PhMeRSi*H by lithium aluminum hydride reduction. Purification of the new system, removal of α-bromonaphthalene and small amounts of other organic products, is best accomplished after reduction.

$$\alpha\text{-NpPhMeSi*Cl} \xrightarrow{\text{RLi}} \alpha\text{-NpPhMeSi*R} \qquad (1)$$

$$\alpha\text{-NpPhMeSi*R} \xrightarrow{\text{Br}_2} \text{PhMeRSi*Br} \qquad (2)$$

$$\text{PhMeRSi*Br} \xrightarrow{\text{LiAlH}_4} \text{PhMeRSi*H} \qquad (3)$$

The first Walden cycle for silicon[7] involved conversion of α-NpPhMeSi*H to its enantiomer *via* chlorination followed by lithium aluminum hydride reduction. For the new systems similar Walden cycles were found. For the new system in which R = neopentyl, $\equiv$Si*H ($[\alpha]\text{D} + 2.5°$) gives $\equiv$Si*Cl ($[\alpha]\text{D} + 5.9°$), which upon reduction furnishes $\equiv$Si*H ($[\alpha]\text{D} - 2.5°$). For the new system in which R = benzhydryl, $\equiv$Si*H($[\alpha]\text{D}$

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(4) L. H. Sommer, P. G. Rodewald, and G. A. Parker, *ibid.*, 18, 821 (1962).

(5) Coupling of α-NpPhMeSi*Cl with RLi has been found to proceed with inversion of configuration (see ref. 3 and 4) in accord with the principle of inversion of configuration for good leaving groups on Si in their reactions with strong nucleophiles, see ref. 1 and 2.

(6) The bromine cleavage of α-NpPhMeSi*-C₆H₄-*p*-OMe proceeds with inversion of configuration: C. Eaborn and O. W. Steward, *Proc. Chem. Soc.*, 59 (1963).

(7) L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.*, **81**, 1013 (1959).