the acid chloride/acid ratio was greater than 20. The acid chloride was then used directly for the perester synthesis.

The peresters were purified by passing them through a column of Woelm activity 1 basic alumina at 0° using ether eluent. This effectively removes all traces of *t*-butyl hydroperoxide. Before each kinetic run the compounds were rechromatographed and all traces of ether removed by pumping under high vacuum. Peroxide contents as determined by iodometric titration were not reproducible (83–92%). A purity of 100% was assumed on the basis of the nmr and infrared spectra and the reproducible kinetic behavior.

The pivalic acid-d_9 and pivaloyl chloride-d_9 were shown to contain less than 1% hydrogen using the nmr spectrum of a solution containing weighed amounts of compound and dioxane. The perester contained less than 2.6% hydrogen in the pivaloyl fragment as judged by the total nmr peak areas in the *t*-butyl region compared to dioxane in known concentration.

Kinetic Methods. The infrared method for measuring the rates utilized the disappearance of the carbonyl stretching band of the perester at 1772 cm^{-1}. The products of the reaction do not absorb at this frequency. Beer's law behavior was verified for this solvent–perester system. About 0.1-ml aliquots of about 0.1 *M* solutions of perester were added to 15 small tubes of Pyrex glass. The tubes were sealed and immersed in a constant temperature bath regulated to ±0.03°, removed at timed intervals, and quenched in ice. The tubes were stored at 0° until the infinity points were taken (ten half-lives). The analyses for duplicate runs were carried out together.

The pseudo-first-order galvinoxyl method utilized the disappearance of the galvinoxyl absorption at 767 mμ. The galvinoxyl solutions (10^{-3} *M*) containing less than a radical equivalent ($n \times$ perester concentration) in Pyrex culture tubes were carefully degassed and sealed under vacuum. Beer's law behavior and the effective path length were determined for each tube. The reaction tubes were immersed in the oil baths for timed intervals, removed and quenched, read in the spectrophotometer, and reimmersed in the bath for a new time increment. Blank solutions of galvinoxyl in chlorobenzene were completely stable over the length of the runs. The blank galvinoxyl solutions in aqueous dioxane showed 14% decomposition over the eight half-life time periods. The runs in this solvent were therefore corrected, point by point, for the behavior of the blank solution. All of the rate plots were linear for more than three half-lives. The zero-order galvinoxyl studies were the same except for the initial perester concentrations.

Product Studies. The gaseous products from the decomposition were collected from breakseal flasks into a calibrated vacuum line. The total gas yield was thus obtained. The composition of the gas mixture was estimated by the sensitivities of the mass spectrometer to the components of the mixture. The *t*-butyl alcohol from the decomposition of the deuterated perester in aqueous dioxane was separated by glpc using a 30 ft × $^5/_8$ in. column packed with 30% SE-30 on Chromosorb W. Its mass spectrum was identical with that of authentic *t*-butyl alcohol.

Acknowledgment. This work was supported by a grant from the Army Research Office, Durham. We are indebted to Dr. C. E. Klopfenstein whose computer program for molecular orbital calculations was modified to include heteroatom and overlap parameters and who assisted us in adapting the Hoffman program to the IBM 360 computer system. We are also grateful to Professor M. Schurr and Professor W. T. Simpson for many penetrating criticisms of this work and to Professor M. Sage for helpful discussions.

The Coupling Reactions of 1-Chlorocyclopentene, 1-Chlorocyclohexene, and 1-Chlorocycloheptene with Phenyllithium. The Question of Cycloallenic Intermediates[1]

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Abstract: In previous work it was postulated that the coupling reactions of 1-chlorocyclopentene and 1-chlorocyclohexene with phenyllithium in ether at 150°, which yield 1-phenylcyclopentene and 1-phenylcyclohexene, proceed *via* an elimination–addition mechanism involving short-lived cycloalkyne intermediates. An alternative mechanism utilizing cycloallenic intermediates was not rigorously ruled out, however. In the present study the reactions of 1-chloro-2-methylcyclopentene, 2-chloro-3-methylcyclopentene, 1-chloro-2-methylcyclohexene, 2-chloro-3-methylcyclohexene, 1-chlorocyclopentene-2,5,5-d_3, 1-chlorocyclohexene-2,6,6-d_3, 1-chlorocycloheptene, and 1-chlorocycloheptene-2,7,7-d_3 with phenyllithium have been examined. In addition, isotopic rate constant ratios, k_H/k_D, were obtained from competition experiments employing 1-chlorocycloalkenes and 1-chlorocycloalkenes-2,*n*,*n*-d_3 (*n*-membered ring). Rate constant ratios for the five-, six-, and seven-membered rings were 3.36 ± 0.40, 5.34 ± 0.40, and 7.16 ± 0.40, respectively. The results of these studies provide compelling evidence that the coupling reactions of 1-chlorocyclopentene, 1-chlorocyclohexene, and 1-chlorocycloheptene with phenyllithium take place predominantly, if not exclusively, by way of an elimination–addition mechanism involving cycloalkyne intermediates.

In 1944, Wittig and Harborth[3] reported that 1-phenylcyclohexene was formed in 5% yield upon heating 1-chlorocyclohexene and phenyllithium in ether at 100°. Later, it was suggested[4] that this reaction might, in a manner analogous to the coupling reactions of aryl halides with aryllithium reagents,[5] proceed *via* an elimination–addition mechanism involving a cyclohexyne intermediate. In an effort to delineate the

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[1] Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Abstracts, p 23N.

[2] National Institutes of Health Predoctoral Fellow, 1964–1967.

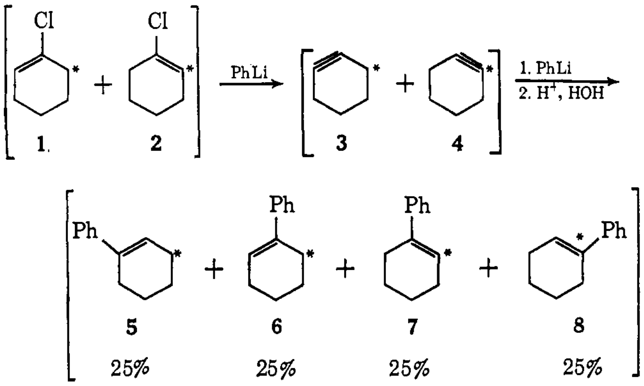
[3] G. Wittig and G. Harborth, *Ber.*, 77, 306 (1944).

[4] F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).

[5] (a) G. Wittig, G. Pieper, and G. Fuhrmann, *Ber.*, **73**, 1193 (1940); (b) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); (c) R. Huisgen and H. Rist, *Naturwissenschaften*, **41**, 358 (1954); (d) R. Huisgen and H. Rist, *Ann.*, **594**, 137 (1955); (e) E. Jenny and J. D. Roberts, *Helv. Chim. Acta*, **38**, 1284 (1955).

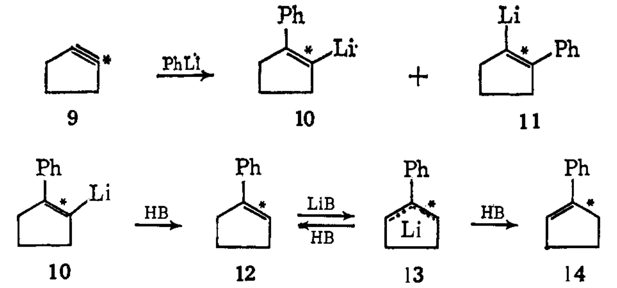
mechanism of substitution, Scardiglia and Roberts[4,6] treated a 1:1 mixture of 1-chlorocyclohexene-6-^{14}C (**1**) and 1-chlorocyclohexene-2-^{14}C (**2**) with phenyllithium in ether at 150°. The 1-phenylcyclohexene which was obtained in 28% yield contained 23% (relative to the total ^{14}C content) of the ^{14}C label in the 1 position (**8**). The fact that ^{14}C was found in the 1 position demonstrates that at least a portion of the substitution product arose from a mechanism other than direct nucleophilic displacement; the percentage of ^{14}C in the 1 position is close to that predicted on the basis of a cyclohexyne hypothesis (Chart I).

Chart I



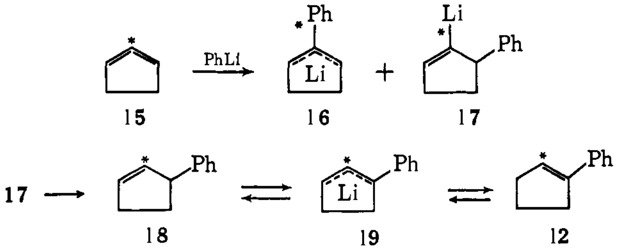
1-Chlorocyclopentene also reacts with phenyllithium at elevated temperatures.[6,7] In a tracer study of this reaction, 1-chlorocyclopentene-1-^{14}C gave rise to 1-phenylcyclopentene in which the starting ^{14}C label was partitioned among the 1 (48.9%), 2 (36.2%), and 5 (14.9%) positions.[6] In the absence of competing or consecutive rearrangement reactions, the ^{14}C should have been distributed equally between the 1 and the 2 positions (**10** and **11**) had cyclopentyne-1-^{14}C (**9**) intervened in the substitution process (Chart II). It has been proposed[6] that a portion of the ^{14}C in the 2 position rearranged to the 5 position by way of base-induced (phenyllithium or lithium ethoxide) allylic isomerization (**10** → **14**, Chart II).

Chart II



Whereas aryl halides can give only one type of 1,2-elimination poduct, arynes, cyclic vinyl halides can, in principle, give either a cycloalkyne or a cycloallene. The patterns of ^{14}C-isotope rearrangement discussed above fit a multistep cycloallenic substitution sequence almost as well as they do a cycloalkyne mechanism. To illustrate, 1,2-cyclopentadiene-2-^{14}C (**15**) would yield organolithium intermediates **16** and **17** in a 1:1 ratio if one-half of the phenyllithium added to the middle and one-half to the ends of the allenic system in **15** (Chart III). Intermediate **16** would ultimately produce 1-phenylcyclopentene-1-^{14}C. Protonation of **17** followed by prototropic rearrangement would afford **12**, which could continue on to **14**. This mechanism cannot be criticized too severely for the necessity of having to rearrange the double bond of **17** into conjugation with the phenyl group (**17** → **12**), since the cyclopentyne mechanism requires similar transformations. The ^{14}C data for 1-chlorocyclohexene can also be explained in terms of a cycloallenic mechanism, provided that the ratio of middle-to-end addition is again 1:1.

Chart III



Roberts and co-workers[6] have stated a definite preference for the cycloalkyne mechanism. Two arguments which they advanced in arriving at this preference were the following. The cycloalkyne hypothesis readily accounts for the *primary pattern* (excluding the prototropic rearrangement of **10** to **14**) of ^{14}C-isotope rearrangement, for phenyllithium should add with equal probability to the two carbons of the cycloalkyne triple bonds (kinetic isotope effects and minor steric differences neglected). It is less obvious why cycloallenes should react with phenyllithium in the manner required by the ^{14}C data. A second objection to cycloallenic intermediates involves a selectivity argument. Were cycloallenic intermediates to intervene, they would have to display some measure of selectivity, for a nonstatistical addition of phenyllithium is called for by the results of the ^{14}C experiments. In view of this selectivity, it is difficult to see why phenyllithium should add to both five- and six-membered ring allenic intermediates to give essentially equal portions of middle-to-end addition. These arguments, though satisfactory from the qualitative point of view, are difficult to translate into quantitative terms. For example, how much more selective should 1,2-cyclohexadiene be than 1,2-cyclopentadiene? Since they should both be highly reactive, might not the selectivity difference be undetectable?

A number of observations in the literature bear directly or indirectly on the question of the suitability of cycloallenes as intermediates in the nucleophilic substitution reactions of nonactivated cyclic olefinic halides. In an attempted synthesis of cyclononyne, Blomquist[8] found that 1-chlorocyclononene reacted with alcoholic potassium hydroxide to give a mixture of cyclononyne and 1,2-cyclononadiene. Moore and Ward[9] have studied acetylene–allene equilibria in C_9-, C_{10}-, and C_{11}-cyclic systems and found that the allene became progressively more stable relative to the isomeric alkynes as the ring size was decreased. A 1,2-cyclononadiene to cyclononyne equilibrium ratio of

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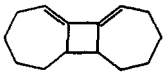
[6] L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 1917 (1965).

[7] L. K. Montgomery and J. D. Roberts, *ibid.*, 82, 4750 (1960).

[8] A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.*, 74, 3643 (1952).

[9] W. R. Moore and H. R. Ward, *ibid.*, 85, 86 (1963).

about 13:1 (potassium *t*-butoxide, *t*-butyl alcohol, 100.3°) was obtained by these authors. Ball and Landor[10] observed that 1-chlorocyclononene and 1-chlorocyclodecene react with sodamide in liquid ammonia to give the corresponding allenes, contaminated with about 15% of the cyclic acetylenes. Under similar reaction conditions 1-chlorocycloheptene and 1-chlorocyclooctene yielded, at least formally, allene dimers (**20** and **21**). Bottini and Schear[11] treated 2-chloro- and 2-bromo-3-(2-hydroxyethoxy)cyclohexene (**22**) with potassium *t*-butoxide in dimethyl sulfoxide and obtained products **23** and **24**. These authors argue effectively that **23** was formed *via* an elimination–addition sequence involving a cycloallenic intermediate and, further, that cycloalkynes were not formed at all in this system. Finally, very recently Wittig[12] has trapped 1,2-cyclohexadiene, generated through the action of potassium *t*-butoxide on 1-bromocyclohexene in dimethyl sulfoxide, using the highly reactive diene 1,3-diphenylbenzo[*c*]furan. Taken as a whole, the above observations strongly suggest the need for additional research on the mechanism of the reactions of 1-chlorocyclohexene and 1-chlorocyclopentene with phenyllithium.



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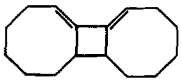

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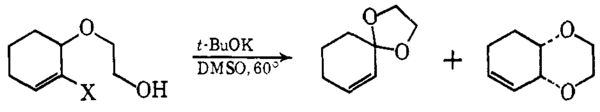

22 **23** **24**

In the present investigation two experimental approaches have been employed in an atempt to unambiguously distinguish between the cycloalkyne and the cycloallene pathways. The first approach might be termed methyl-group blocking experiments. 2-Methylcycloalkanones, when treated sequentially with phosphorus pentachloride and base, yield mixtures of 1-chloro-2-methylcycloalkenes and 1-chloro-*n*-methylcycloalkenes (*n*-membered ring). The former halides cannot give rise to cycloalkynes, while the latter can. A simple mechanistic test is thus provided by examining the reactions, or lack thereof, of the two types of chlorides with phenyllithium. Moreover, the methyl groups of the 1-chloro-*n*-methylcycloalkenes serve as structural labels for the observation of any rearrangement which accompanies substitution. The methyl-group blocking experiments, though extremely classical in nature, prove to be an effective mechanistic tool, particularly in view of the relative ease with which they can be carried out experimentally. In a second approach, deuterium-labeled vinyl chlorides have been used to detect rearrangement and to probe the timing of the bond-breaking processes that lead to products.

Results and Discussion

General. The olefinic chlorides required for this study were prepared from appropriate ketones by way of a two-step sequence. In the first, a simple ketone, a cycloalkanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$, or a 2-methylcycloalkanone was treated with phosphorus pentachloride in methylene chloride, affording a mixture of the desired olefinic chloride(s) and the *gem*-dichloride. The crude chloride mixtures were treated with potassium *t*-butoxide in *t*-butyl alcohol, sodium methylsulfinyl carbanion in dimethyl sulfoxide, or potassium *t*-butoxide in dimethyl sulfoxide in order to dehydrohalogenate the *gem*-dichlorides. The deuterated cycloalkanones were prepared from cycloalkanones by base-catalyzed proton–deuteron exchange with deuterium oxide. Authentic samples of possible olefinic chloride–phenyllithium substitution products were synthesized following standard procedures.

The previously reported[4,6,7] coupling reactions of 1-chlorocyclopentene and 1-chlorocyclohexene with phenyllithium afforded 1-phenylcyclopentene and 1-phenylcyclohexene in 25–35% yields. It has been found that 1-chlorocycloheptene reacts with phenyllithium under similar reaction conditions to give 1-phenylcycloheptene; typical yields were somewhat higher. In an effort to determine whether these substitution reactions are a general reaction of olefinic chlorides, *trans*-3-chloro-2-pentene and phenyllithium were subjected to the standard reaction conditions. Analysis of the reaction products revealed that 55% of the starting chloride had been consumed, but that neither couplng products (*trans*- and *cis*-2-phenyl-2-pentene, *trans*- and *cis*-3-phenyl-2-pentene, 2-phenyl-1-pentene) nor acetylenic elimination products (1- and 2-pentyne) were present. These findings could be rationalized in a variety of ways; an extended discussion of such possibilities would seem of doubtful value. *cis*-3-Chloro-2-pentene would be a better model for the cyclic chlorides, and it is possible that an examination of its reaction with phenyllithium might be more revealing. Considering the equivocacy of the *trans* isomer results, however, additional effort was not expended on this aspect of the coupling reactions.

The C$_5$ Ring System. An ether solution which was 0.072 *M* in 1-chloro-2-methylcyclopentene and 0.76 *M* in phenyllithium was sealed in a stainless steel bomb and heated at 150° for 1.3 hr.[13] The cooled reaction mixture was poured into water; the resulting organic reaction products were separated and quantitatively analyzed. A summary of products of interest is reported in Table I. Little or no (2% or less) coupled products were observed, indicating that an olefinic proton is required to achieve substitution.

Only 39% of the initial 1-chloro-2-methylcyclopentene was recovered. Independent of what the process or processes were that destroyed the starting material, it is interesting to note that a minimum[14] of 40% of the chlorine in the starting olefin ended up as chloride ion in the aqueous wash solutions. About 21% of the chlorine in the initial 1-chloro-2-methylcyclopentene was not accounted for. Presumably nonvolatile, chlorine-containing products, perhaps polymer, were also formed.

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(10) (a) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); (b) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

(11) A. T. Bottini and W. Schear, *J. Am. Chem. Soc.*, 87, 5802 (1965).

(12) G. Wittig and P. Fritze, *Angew. Chem. Intern. Ed. Engl.*, **5**, 856 (1966).

(13) All of the coupling reactions in this study were conducted at (150 ± 10)° for a period of 1.3 hr. The concentrations of the reactants varied somewhat from experiment to experiment.

(14) A large quantity of bromide ion which came from the phenyllithium preparation was also present, making a precise chloride ion analysis difficult. Control experiments indicated that the chloride analyses reported here are low by several per cent (8–12% of the total chloride ion).

Table I. Reaction of 1-Chloro-2-methylcyclopentene with Phenyllithium[a]

Reactant or product	Reactant, mmoles	Product, mmoles
1-Chloro-2-methylcyclopentene	7.23	2.80
3-Methyl-1-phenylcyclopentene and 3-methyl-2-phenylcyclopentene	0[b]	<0.16[c]
1-Methylcyclopentene	0[b]	Trace
Chloride ion	0[b]	2.85

[a] Conducted in 100 ml of anhydrous ether at (150 ± 10)° for 1.3 hr. [b] No analysis was made. Presumed to be absent. [c] Trace of unidentified component(s).

One final product of interest was the trace amount of 1-methylcyclopentene. Since it was not in the 1-chloro-2-methylcyclopentene, it most likely arose by way of metal–halogen interconversion.

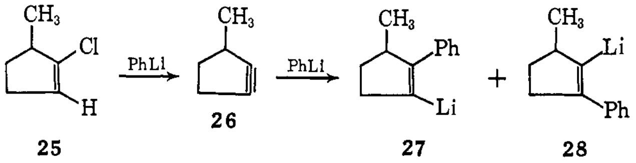
When 2-chloro-3-methylcyclopentene was heated with phenyllithium, 85% reaction occurred (Table II).

Table II. Reaction of 2-Chloro-3-methylcyclopentene with Phenyllithium

Reactant or product	Reactant, mmoles	Product, mmoles
2-Chloro-3-methylcyclopentene	15.9	2.4
3-Methyl-2-phenylcyclopentene	0[b]	2.00
3-Methyl-1-phenylcyclopentene	0[b]	2.09
3-Methylcyclopentene	0[b]	Trace
Chloride ion	0[b]	10.54

[a] Conducted in 140 ml of ether at (150 ± 10)° for 1.3 hr. [b] No analysis was made. Presumed to be absent.

Two substitution products were detected and isolated employing glpc. One was unequivocally identified as 3-methyl-2-phenylcyclopentene. The chromatographic retention time behavior of the other product was identical with that of a nonseparable mixture of 3-methyl-1-phenylcyclopentene and 4-methyl-1-phenylcyclopentene, which was prepared independently starting from 3-methylcyclopentanone. Moreover, the nmr and infrared spectra of the second substitution product were similar, though not identical, with those of the olefin mixture. One noteworthy spectral difference was that the nmr vinyl proton absorption of the coupled product was a crude doublet, while the same absorption region of the olefin mixture was broader and more complex. It would not be unreasonable to infer from this that the substitution product was predominantly one isomer, 3-methyl-1-phenylcyclopentene, the product that would be expected (**25** → **26** → **27** + **28**) for an elimination–addition substitution mechanism involving a 3-methylcyclopentyne intermediate **26**. The fact that 3-methyl-2-phenylcyclopentene and 3-methyl-1-phenylcyclopentene were obtained in roughly equal quantities (Table II) lends additional upport to the postulated intermediacy of 3-methylcyclopentyne. Slight steric differences in the transition states for the formation of organolithium intermediates **27** and **28** are probably responsible for the slight preferential formation of 3-methyl-1-phenylcyclopentene.



One aspect of the 2-chloro-3-methylcyclopentene study that is somewhat disturbing is that no allylic isomerization of the substitution products was noted. Although limited isomerization of 3-methyl-1-phenylcyclopentene to 4-methyl-1-phenylcyclopentene would not have been discerned, prototropic rearrangement of 3-methyl-2-phenylcyclopentene to 2-methyl-1-phenylcyclopentene would have been easily detected by glpc. It could be argued that base-catalyzed allylic isomerization of 3-methyl-2-phenylcyclopentene is slow owing to the fact that proton removal must occur at a tertiary carbon; such a rationalization is not entirely satisfying. Accordingly, the mechanism of coupling was probed by a second method.

The reaction of 1-chlorocyclopentene-2,5,5-d_3 with phenyllithium provided coupled product in only 11% yield, suggesting that a kinetic isotope effect was operative. About 65% of the starting chloride was recovered. The infrared and nmr spectra of the recovered olefin were identical with those of the starting material. Proton nmr analysis of the substitution product indicated that 0.14 ± 0.03 deuterons and 1.84 ± 0.20 deuterons resided in olefinic and saturated ring positions, respectively. In order to gain an indication as to how much of the coupled product existed as some form of an organolithium species at the end of the reaction, 1-chlorocyclopentene was treated with phenyllithium, and the resultant products were treated with deuterium oxide. An average of 0.20 ± 0.03 deuteron was incorporated into the olefinic position; a maximum of 0.2 deuteron was present in the saturated positions. Mass spectral analysis of the benzene–benzene-d_1 showed that about 12% of the initial phenyllithium survived the reaction. In Table III the experimental deuterium distribution in the 1-chlorocyclopentene-2,5,5-d_3 coupled product is compared to calculated distributions based on four alternative mechanistic hypotheses: cyclopentyne-3,3-d_2 intermediate, no allylic isomerization; cyclopentyne-3,3-d_2 intermediate, allylic isomerization as required by the ^{14}C-tracer study;[6] 1,2-cyclopentadiene-1,3-d_2 intermediate, sufficient isomerization to obtain 1-phenylcyclopentene (*vide supra*); 1,2-cyclopentadiene-1,3-d_2 intermediate, allylic isomer-

Table III. Reaction of 1-Chlorocyclopentene-2,5,5-d_3 with Phenyllithium[a]

Observation or hypothetical model	Deuterium[b] Olefinic	Deuterium[b] Saturated
Observed	0.14 ± 0.03[c]	1.84 ± 0.20[c]
Cyclopentyne-3,3-d_2, no isomerization	0	2.00
Cyclopentyne-3,3-d_2, isomerization	0.15	1.55
1,2-Cyclopentadiene-1,3-d_2, limited isomerization	0.50	1.00
1,2-Cyclopentadiene-1,3-d_2, isomerization	0.43	0.93

[a] Conducted in ether at (150 ± 10)° for 1.3 hr. [b] Average number of deuterons per position per molecule. [c] Student's distribution, 99.5% confidence limit.

ization as required by the ^{14}C-tracer study.[6] Clearly, the cyclopentyne-3,3-d_2 isomerization hypothesis provides the best fit to the data. The glaring inability of the 1,2-cyclopentadiene-1,3-d_2 hypotheses to accommodate the data is also significant.

The kinetic isotope effect was examined in a competition experiment employing 1-chlorocyclopentene and 1-chlorocyclopentene-2,5,5-d_3 in a 2.7:1 molar ratio. So little deuterium was present in the coupled product that an isotope effect on *coupling* could not be reliably determined directly from product composition. The unreacted chlorides could be accurately assayed, however. From the initial and final quantities of 1-chlorocyclopentene and 1-chlorocyclopentene-2,5,5-d_3, a rate constant ratio, k_H/k_D, for the *disappearance of starting material* of 3.36 ± 0.40 was calculated using the standard formula.[15] In applying this formula, the usual assumptions[15] were made, namely that the rate expressions for the two competing reactions were first order in substrate but otherwise differed only in the values of the specific rate constants k_H and k_D.

The value of k_H/k_D is quite large, considering the temperature at which the competition experiment was conducted. If merely the zero-point energies of the CH and CD stretching vibrations were lost in going to the coupling reaction transition states, the maximum expected rate constant ratio at 150° would be about 3.8[16,17] Even if k_H/k_D for substitution was lower than the measured ratio, it is obvious that it was sizeable in view of the modicum of deuterium that was incorporated into the product. Consequently, the competition experiment provides valuable evidence in support of the proposed elimination–addition mechanism. The magnitude of the isotope effect and the fact that 1-chlorocyclopentene-2,5,5-d_3 was recovered unmodified make it clear that the rate-determining step in substitution is an irreversible metallation at the olefinic proton (deuteron) position or, alternatively, concerted elimination to cyclopentyne (cyclopentyne-3,3-d_2).

The C$_6$ Ring System. Preparative glpc could not be conveniently employed to separate 1-chloro-2-methylcyclohexene and 2-chloro-3-methylcyclohexene. A mixture of the two isomers was treated with phenyllithium. In Table IV a summary of reactants and products is displayed. The product distribution appears to be very much the same as with the methyl-labeled chlorocyclopentenes. About 38% of the 1-chloro-2-methylcyclohexene reacted. No 2-methyl-1-phenylcyclohexene was observed, implying that substitution products were not formed from 1-chloro-2-methylcyclohexene. If the coupling of 2-chloro-3-methylcyclohexene with phenyllithium followed a route involving 3-methylcyclohexyne, 3-methyl-2-phenylcyclohexene and 3-methyl-1-phenylcyclohexene should have been produced in a 1:1 ratio. A ratio close to this value was observed experimentally. As was the case with the products from 2-chloro-3-methylcyclopentene, the 1-phenyl isomer was favored slightly.

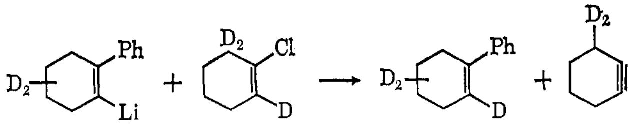
Table IV. Reactions of 1-Chloro-2-methylcyclohexene and 2-Chloro-3-methylcyclohexene with Phenyllithium[a]

Reactant or product	Reactant, mmoles	Product, mmoles
1-Chloro-2-methylcyclohexene	28.4	17.7
2-Chloro-3-methylcyclohexene	17.7	3.99
3-Methyl-2-phenylcyclohexene	0[b]	4.00
3-Methyl-1-phenylcyclohexene	0[b]	4.35
1-Methylcyclohexene	0[b]	Trace
3-Methylcyclohexene	0[b]	Trace
Chloride ion	0[b]	23.4

[a] Conducted in 210 ml of ether at (150 ± 10°) for 1.3 hr. [b] No analysis made. Presumed to be absent.

1-Chlorocyclohexene-2,6,6-d_3 and phenyllithium gave a deuterium-labeled substitution product in 13% yield. Unreacted olefinic chloride was recovered and was found to be unchanged. Analysis of the deuterium distribution in the coupled product showed, as anticipated, that an average of 1.93 ± 0.11 deuterons was located in the saturated ring positions. Quite unexpected, however, was the finding that 0.82 ± 0.09 deuteron resided in the olefinic position. Mass spectral analysis of the benzene from the reaction revealed that only 7.0 mmoles of benzene-d_1 was formed. About 20.2 mmoles of 1-chlorocyclohexene-2,6,6-d_3 reacted. A plausible explanation of these results would be that a large primary kinetic isotope effect retarded the rate of the elimination–addition pathway to such an extent that direct nucleophilic substitution could effectively compete for the 1-chlorocyclohexene-2,6,6-d_3. Isotope rate constant measurements indicate that this is not the case.

The kinetic isotope effect in the C$_6$ system was explored utilizing the competition method. A 3:1 mixture of 1-chlorocyclohexene and 1-chlorocyclohexene-2,6,6-d_3 afforded a substitution product possessing nmr and infrared spectra which were virtually indistinguishable from nondeuterated 1-phenylcyclohexene. A k_H/k_D of 5.34 ± 0.40 was calculated, based on the consumption of olefinic chlorides. It is clear from these observations that 1-chlorocyclohexene-2,6,6-d_3 does not react with phenyllithium by way of direct nucleophilic displacement. About the only way to bring the 1-chlorocyclohexene-2,6,6-d_3 product study and the k_H/k_D measurement into compatibility is to assume that coupling takes place *via* a cyclohexyne-3,3-d_2 (**32**) intermediate and that the organolithium compounds which result from phenyllithium addition (**29**) react preferentially with the substrate (**29** + **30** → **31** + **32**). If the reaction is autocatalytic, k_H/k_D cannot be calculated in the usual manner.[15] Nevertheless, qualitatively it is clear that a large isotope effect operates on the coupling reaction.



29 **30** **31** **32**

The C$_7$ Ring System. Methyl-group blocking experiments were not carried out on a C$_7$ system. In order to see if substitution occurs with cycloheptenyl chlorides, 1-chlorocycloheptene-2,7,7-d_3 was heated with phenyllithium under the standard reaction con-

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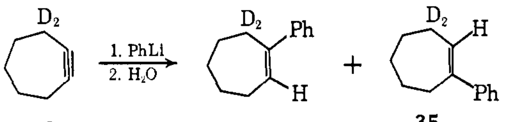
(15) G. A. Russell in "Technique of Organic Chemistry," Vol. VIII, Part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 343.

(16) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, p 20.

(17) Calculation based on CH and CD stretching frequencies (infrared data) of 3077 and 2294 cm^{-1}.

ditions. Substitution product was obtained in 15% yield, which is somewhat higher than with the C_5 and C_6 deuterated chlorides. Proton nmr analysis of the coupled product indicated the presence of 0.17 ± 0.02 deuteron per molecule in the olefinic position and 1.96 ± 0.12 deuterons per molecule in the saturated ring positions. Since the saturated proton region of the nmr spectrum of 1-phenylcycloheptene consisted of complex absorption extending continuously from 1.1 to 2.9 ppm downfield from tetramethylsilane, it was not possible[18] to determine the position(s) of the two deuterons on the cycloheptene ring. The deuteron nmr spectrum of the substitution product,[19] however, revealed two types of aliphatic deuterons, centered at 2.80 and 2.50 ppm. The areas of the deuteron absorption peaks were approximately equal, the downfield peak being slightly the larger. These data provide excellent evidence that substitution takes place by way of a cycloheptyne-3,3-d_2 (**33**) intermediate.



33 **34** **35**

The k_H/k_D for competition between 1-chlorocycloheptene and 1-chlorocycloheptene-2,7,7-d_3 was 7.16 ± 0.40. As in the C_5 and C_6 systems, the product contained little deuterium. At least two factors might reasonably be responsible for the unusually large magnitude of the rate constant ratio. First, it has been reported that tunneling is important in certain bimolecular elimination reactions and that k_H/k_D is increased accordingly.[20] Second, a variety of detailed elimination mechanisms can be envisioned which involve multicenter transition states. With such mechanisms the CH and CD stretching *and bending* frequencies might both be important in determining the magnitude of the isotope effect.[21]

The Question of Cycloallenic Intermediates. The experimental results presented in this paper in consort with the earlier ^{14}C-tracer studies[6] demonstrate beyond reasonable doubt that the coupling reactions of 1-chlorocyclopentene, 1-chlorocyclohexene, and 1-chlorocycloheptene with phenyllithium proceed predominantly, if not exclusively, by way of elimination–addition mechanisms involving cycloalkyne intermediates. It is clear, nonetheless, that the olefinic chlorides enter into reactions other than substitution. For example, in no case was there a 1:1 molar correspondence between chloride consumed and coupled product formed. 1-Chloro-2-methylcyclopentene and 1-chloro-2-methylcyclohexene underwent significant reaction, despite the fact that they possessed no olefinic protons. It is difficult to say whether or not cycloallenic intermediates might be involved in these side reactions.

Returning to the findings of Wittig,[12] Bottini,[11] and Landor,[10] it appears that 1-halocycloalkenes and strongly basic nucleophiles can give rise to either cycloalkynes or cycloallenes, depending upon the particular halide, base, and reaction conditions employed. Factors such as the relative rates of cycloalkyne and cycloallene formation, the rate of cycloalkyne–cycloallene interconversion, and cycloalkyne–cycloallene relative stability are probably important in determining which reaction path is followed in a given system. Unfortunately, little is known concerning the above factors. In preliminary results[22] from a study of the quantitative conformational analyses of C_8, C_9, and C_{10} cycloalkynes and cycloallenes (extended Wiberg[23] scheme), we have found that the energies of the conformations of minimum energy in these systems are complex composites of bond angle, torsional, and nonbonded energy terms. Accordingly, it is doubtful that the cycloalkyne–cycloallene equilibrium data of Moore and Ward[9] provide reliable insight into the relative stabilities of cycloalkynes and cycloallenes in smaller ring systems. One interesting point that has been noted concerns the general difficulty of placing a triple bond in the lower members of the medium-sized rings. For simple geometrical reasons alone, the collinear, four-atom grouping of a strain-free triple bond cannot be placed in a carbocyclic ring containing less than nine carbon atoms without introducing substantial bond angle distortions at one or more positions. Conformational analysis of the C_8–C_{10} cycloalkynes have made it evident that the restrictions that the linear four-atom acetylenic array impose on a cyclic system are not as severe as might be expected on the basis of geometrical considerations. This is true owing to the fact that C—C≡C bond angles are relatively easy to distort; the bending force constants for C—C≡C bond angles are about one-third those for C—C—C bond angles.[24] It is not clear how important a role these force constant differences might play in determining conformational preferences and relative cycloalkyne stabilities in the smallest cycloalkynes, for it is known that highly strained systems cannot be satisfactorily treated using the usual quantitative conformational analysis schemes.

Experimental Section

Boiling points are uncorrected. Nmr and infrared spectra were routinely recorded and are assumed to be in satisfactory agreement with authentic or predicted spectra when they are not explicitly discussed. The nmr spectra were obtained from dilute chloroform-d_1 solutions using a Varian Associates A-60 spectrometer. Chemical shifts are reported as parts per million displacements from tetramethylsilane as an internal standard. Infrared spectra were generally recorded on both Perkin-Elmer Model 137 and Model 137-G (near-infrared) Infracord spectrometers. Quantitative glpc determinations were carried out on an F & M Scientific Model 609 flame-ionization gas chromatograph equipped with a Minneapolis-Honeywell recorder (Model Y153-999) fitted with a Disc Instruments integrator. All of the columns used with the F & M instrument were stainless steel and 8 ft in length (0.25 in. o.d.). The columns and their designations are: 20% silicone gum GE XE-60 on 60–80 mesh Chromosorb P (XEA); 20% Carbowax 20M on 60–80 mesh Chromosorb P (20CWA); 10% Carbowax 20M on 60–80 mesh Diatoport S(10CWA). Preparative glpc was conducted on a F & M Model 720 gas chromatograph fitted with 8-ft (0.375-in. o.d.) stainless steel columns. The columns were: 20% silicone gum GE XE-60 on 60–80 mesh Chromosorb P (XEP); 20% Carbowax 20M on 60–80 mesh Chromosorb P (CWP). Mass

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(18) This was also true in the case of the coupling products from 1-chlorocyclopentene-2,5,5-d_3 and 1-chlorocyclohexene-2,6,6-d_3.

(19) L. K. Montgomery, A. O. Clouse, A. M. Crelier, and L. E. Applegate, *J. Am. Chem. Soc.*, in press.

(20) V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **83**, 593 (1961).

(21) Reference 16, p 21.

(22) L. K. Montgomery, D. W. Garrett, and G. J. Eubanks, unpublished results.

(23) K. B. Wiberg, *J. Am. Chem. Soc.*, **87**, 1070 (1965).

(24) (a) J. H. Schachtschneider and R. G. Synder, *Spectrochim. Acta*, **19**, 117 (1963); (b) J. L. Duncan, *ibid.*, **20**, 1197 (1964).

spectra were recorded on a Consolidated Electrodynamics Corp Model 21-260 mass spectrometer.

Cyclohexanone-2,2,6,6-d_4. A solution consisting of 45 g (0.46 mole) of cyclohexanone, 80 g (4.00 moles) of deuterium oxide (99.8%), 10 ml of triethylamine, and 400 ml of anhydrous dioxane was refluxed for 48 hr. Deuterium oxide, water, triethylamine, and dioxane were removed by distillation. The exchange was repeated four more times. Final distillation afforded 27.1 g (58%) of cyclohexanone-2,2,6,6-d_4, bp 148–153°.

Cyclopentanone-2,2,5,5-d_4 was prepared by Mr. D. Armstrong in the laboratories of V. J. Shiner, Jr., following a procedure similar to the one outlined above for cyclohexanone-2,2,6,6-d_4. We wish to thank Professor Shiner for lending us this material.

Olefinic Chlorides. The preparation of 1-chloro-2-methylcyclopentene and 2-chloro-3-methylcyclopentene illustrates the general procedure which was employed for the preparation of olefinic chlorides from ketones. A solution of 39.2 g (0.40 mole) of 2-methylcyclopentanone in 45 ml of methylene chloride was added slowly to 103 g (0.50 mole) of phosphorus pentachloride in 530 ml of methylene chloride (4–5°). The solution was stirred for 1 hr at this temperature, allowed to warm to 18° over a 1-hr period, and poured onto crushed ice. The methylene chloride layer was separated and washed thoroughly with 40% sodium hydroxide solution and water. Removal of the solvent by distillation left a 26.4-g mixture of 1-chloro-2-methylcyclopentene, 2-chloro-3-methylcyclopentene, and 1,1-dichloro-2-methylcyclopentane. The latter compound was dehydrohalogenated following method 1.

Dehydrohalogenation Method 1. The crude chloride mixture was added dropwide over a 5-min period to a 0.34 *M* solution of methylsulfinyl carbanion (4.0 g of sodium hydride) in dimethyl sulfoxide (500 ml). The rate of addition was such that the temperature stayed within the range 18–32°. The solution was stirred an additional 5 min at 24° and poured into water. The reaction products were taken up in methylene chloride; the extract was washed thoroughly with water. Distillation afforded 8.36 g (18% based on ketone) of 1-chloro-2-methyl- and 2-chloro-3-methylcyclopentene (45:55), bp 120–123°. The two chlorides were separated employing preparative glpc (XEP, 125°, 200 cc/min).

In general the olefinic chlorides were purified by preparative glpc, stored in sealed ampoules under refrigeration, and redistilled immediately prior to use. Typical purity after distillation as assessed by glpc was 99% or greater.

1-Chloro-2-methylcyclohexene and 2-Chloro-3-methylcyclohexene. 2-Methylcyclohexanone (44.0 g, 0.397 mole), phosphorus pentachloride (103 g, 0.49 mole), and sodium methylsulfinyl carbanion (method 1; 7.2 g, 0.30 mole of sodium hydride in 300 ml of dimethyl sulfoxide) provided 7.3 g (14%; 99% purity by glpc; 20 CWA, 100°, 33 cc/min) of the two olefinic chlorides, bp 58–63° (23 mm) [lit.[25] bp 41–42° (8 mm)]. A 65:35 mixture of isomers was indicated by glpc. A 65:35 mixture was also inferred from nmr. The predominant isomer was 1-chloro-2-methylcyclohexene.

1-Chlorocyclopentene. Cyclopentanone (44.0 g, 0.52 mole), phosphorus pentachloride (135 g, 0.65 mole), and potassium *t*-butoxide (method 2;[6] 12.4 g, 0.32 equiv of potassium in 400 ml of *t*-butyl alcohol) provided 16.3 g of crude 1-chlorocyclopentene, bp 99–108°, 93% purity by glpc (29%). Chromatographed material (CWP, 120°, 150 cc/min) was redistilled, bp 102–103° (lit.[6] bp 102–103°).

1-Chlorocyclohexene. Cyclohexanone (19.6 g, 0.200 mole), phosphorus pentachloride (49.5 g, 0.238 mole), and potassium *t*-butoxide (method 2;[6] 6.2 g, 0.159 equiv of potassium in 200 ml of *t*-butyl alcohol) provided 7.9 g of crude 1-chlorocyclohexene, bp 139–141°, 95% purity by glpc (33%). Chromatographed material (CWP, 145°, 150 cc/min) was redistilled, bp 140–141° (lit.[26] bp 142–143°).

1-Chlorocycloheptene. Cycloheptanone (44.8 g, 0.400 mole) and phosphorus pentachloride (104 g, 0.500 mole) gave 41.9 g of crude chlorides which was treated with base following method 3.

Dehydrohalogenation method 3 was very similar to method 1, the principal difference being that potassium *t*-butoxide (MSA Research Corp.) was employed as the base. The chlorides from cycloheptanone were added to a solution of 15 g of potassium *t*-butoxide in 190 ml of dimethyl sulfoxide. About 17 g (80% 1-chlorocycloheptene; 24%) of dehydrohalogenation products, bp 150–176°, were obtained. The chromatographed material (CWP, 140°, 150 cc/min) was redistilled, bp 55.0–55.5° (12 mm) [lit.[10] bp 54–58° (14 mm)].

1-Chlorocyclopentene-2,5,5-d_3. Cyclopentanone-2,2,5,5-d_4 (45.5 g, 0.517 mole), phosphorus pentachloride (135 g, 0.649 mole), and potassium *t*-butoxide (method 2;[6] 45 g, 1.15 equiv of potassium in 875 ml of *t*-butyl alcohol) provided 17.9 g of olefinic chloride (93% purity; 31%), bp 103–105°. Chromatographed (CWP, 120°, 150 cc/min) and redistilled, bp 103–104°, 1-chlorocyclopentene-2,5,5-d_3, $n^{25.5}$D 1.4379, contained 3.00 ± 0.06 deuterons/molecule, as assessed by proton nmr (benzene, quantitative internal standard). There was no visually discernible absorption in the olefinic proton region.

1-Chlorocyclohexene-2,6,6-d_3. Cyclohexanone-2,2,6,6-d_4 (26.6 g, 0.261 mole), phosphorus pentachloride (70.7 g, 0.340 mole), and potassium *t*-butoxide (method 2;[6] 10 g, 0.26 equiv of potassium in 350 ml of *t*-butyl alcohol) provided 23.8 g of olefinic chloride (62% purity; 46%), bp 139–151°. Chromatographed (CWP, 145°, 150 cc/min) and redistilled, bp 139–141°, 1-chlorocyclohexene-2,6,6-d_3, $n^{25.5}$D 1.4797, contained 3.00 ± 0.06 deuterons/molecule, as assessed by proton nmr (biphenyl, quantitative internal standard). There was no visually discernible absorption in the olefinic proton region.

1-Chlorocycloheptene-2,7,7-d_3 was available from another study.[19] Chromatographed (CWP, 140°, 150 cc/min) and redistilled, bp 52–53° (11 mm), 1-chlorocycloheptene-2,7,7-d_3, $n^{25.6}$D 1.4859, contained 2.89 ± 0.06 deuterons/molecule, as assessed by proton nmr (biphenyl, quantitative internal standard). There was no visually discernible absorption in the olefinic proton region.

***trans*-3-Chloro-2-pentene.** 3-Pentanone (137.6 g, 1.60 moles) and phosphorus pentachloride (416 g, 2.00 mole) gave about 100 g of a mixture of *trans*- and *cis*-3-chloro-2-pentene and 3,3-dichloropentane. The *trans* isomer, bp 92–93° (lit.[27] bp 92–93°), could be easily obtained in high purity by fractional distillation and was used in the attempted coupling experiment.

Phenyllithium Coupling Reactions. The reactions of 1-chloro-2-methylcyclohexene and 2-chloro-3-methylcyclohexene with phenyllithium illustrate the general procedure. A solution consisting of 3.692 g (0.0284 mole) of 1-chloro-2-methylcyclohexene, 2.308 g (0.0177 mole) of 2-chloro-3-methylcyclohexene, and 0.221 mole of phenyllithium[28] in 210 ml of ether was placed in a 300-ml stainless steel bomb, sealed, and heated at 150 ± 10° for 1.3 hr. The bomb was cooled in air (20 min), ice water (25 min), and Dry Ice-acetone (10 min), vented, and allowed to warm to room temperature. The reaction products were washed out of the bomb with water and ether. The ether layer was separated, washed with two 100-ml portions of water, and dried twice over 7-g quantities of anhydrous calcium chloride. Most of the ether was removed by distillation, and the reaction products were analyzed by glpc. Cyclohexanone was employed as an internal standard for low-boiling components (20 CWA, 100°, 33 cc/min) and N,N-dimethylaniline for high-boiling components (20 CWA, 225°, 30 cc/min). Detector response conversion factors were determined for most compounds. The responses of 1-chloro-2-methylcyclohexene and 2-chloro-3-methylcyclohexene were assumed to be equal. A mixture of 3-methyl-1-phenylcyclohexene and 4-methyl-2-phenylcyclohexene (*vide infra*) was used to estimate the conversion factor for 3-methyl-1-phenylcyclohexene. A summary of the analyses for key reaction products is provided in Table IV. Benzene, ethylbenzene, and biphenyl were also present. The substitution products were isolated employing glpc (XEP, 205°, 200 cc/min). 3-Methyl-2-phenylcyclohexene was identified by comparing its nmr and infrared spectra with those of an authentic sample. The second product, judged to be 3-methyl-1-phenylcyclohexene, possessed characteristic infrared absorption bands at 1639, 1597, and 1572 cm^{-1} (*vide infra*). The nmr spectrum consisted of complex absorption (5.0 protons, assigned) from 7.5 to 6.8, complex absorption (0.83 proton) from 6.00 to 5.92, and complex absorption (10.3 protons) from 2.6 to 0.8 which included a well-defined doublet (6.5 cps) at 1.04 (*vide infra*). The chloride analysis in Table IV was carried out following a procedure outlined by Kolthoff and Stenger.[29]

1-Chloro-2-methylcyclopentene and Phenyllithium. 1-Chloro-2-methylcyclopentene (0.8382 g, 0.00723 mole) and 100 ml of 0.76 *M*

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(25) N. A. Domnin, *J. Gen. Chem. USSR*, 10, 1939 (1940); *Chem. Abstr.*, 35, 3979^5 (1941).

(26) M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 648 (1960).

(27) A. L. Henne and E. G. Dewitt, *J. Am. Chem. Soc.*, 70, 1548 (1948).

(28) (a) R. G. Jones and H. Gilman, *Org. Reactions*, 6, 339 (1951); (b) H. Gilman, *Bull. Soc. Chim. France*, 1356 (1963).

(29) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p 272.

phenyllithium (0.076 mole) in ether was heated at 150 ± 10° for 1.3 hr. A summary of the reaction products is provided in Table I.

2-Chloro-3-methylcyclopentene and Phenyllithium. 2-Chloro-3-methylcyclopentene (1.8476 g, 0.01593 mole) and 140 ml of 1.19 *M* phenyllithium (0.167 mole) in ether were heated at 150 ± 10° for 1.3 hr. A summary of the reaction products is provided in Table II (20 CWA, 70°, 200°, 35 cc/min). The substitution products were isolated by glpc (XEP, 125°, 200 cc/min). The product identified as 3-methyl-2-phenylcyclopentene possessed characteristic infrared absorption bands at 1618, 1597, and 1571 cm^{-1} (*vide infra*). The nmr spectrum consisted of complex absorption (5.0 protons, assigned) from 7.5 to 6.9, complex absorption (0.85 proton) from 6.10 to 5.93, complex absorption (8.15 protons) from 6.10 to 5.93, and complex absorption (8.15 protons) from 2.9 to 1.5, which included a doublet (7 cps) at 1.07 (*vide infra*). The product identified as 3-methyl-1-phenylcyclopentene possessed characteristic infrared absorption bands at 1623, 1597, and 1572 cm^{-1} (*vide infra*). The nmr spectrum consisted of complex absorption (5.0 protons, assigned) at 7.5–6.9, a crude doublet (~2 cps, 0.7 proton) at 6.07, complex absorption at 3.2–1.3 (8.2 protons), and a doublet (7 cps, 2.2 protons) at 1.08 (*vide infra*).

1-Chlorocyclopentene-2,5,5-d_3 and Phenyllithium. 1-Chlorocyclopentene-2,5,5-d_3 (9.0048 g, 0.8538 mole) and 210 ml of 0.98 *M* phenyllithium (0.203 mole) in ether were heated at 150 ± 10° for 1.3 hr. The reaction mixture containing 5.88 g (65.3%; 20 CWA, 70°, 35 cc/min) of 1-chlorocyclopentene-2,5,5-d_3 and 1.31 g (10.7%; 20 CWA, 225°, 35 cc/min) of deuterated 1-phenylcyclopentene. Both compounds were isolated utilizing preparative glpc. The nmr and infrared spectra of the recovered chloride were virtually identical with those of the starting material. Proton nmr analysis of the deuterated 1-phenylcyclopentene indicated the presence of 0.14 ± 0.03 deuteron and 1.84 ± 0.20 deuterons in the olefinic and saturated ring positions, respectively. The phenyl protons were used as a quantitative internal standard for the analysis.

The quoted error was calculated from six integrations using a Student's t distribution analysis and employing a 99.5% confidence limit.

1-Chlorocyclopentene and Phenyllithium. Deuterium Oxide Quenching. 1-Chlorocyclopentene (8.179 g, 0.0798 mole) and 240 ml of 0.85 *M* phenyllithium (0.204 mole) in ether were heated at 150 ± 10° for 1.3 hr. Exactly 50.0 ml of deuterium oxide was added to the reaction products. The products were then processed in the usual manner. The reaction products included 3.04 g (37.5%; 20 CWA, 70°, 35 cc/min) of 1-chlorocyclopentene and 2.76 g (23.7%; 20 CWA, 225°; 35 cc/min) of 1-phenylcyclopentene. Analysis of the benzene (glpc, mass spectrometry) indicated that 12.4% of the starting phenyllithium was present at the end of the reaction. Proton nmr analysis of glpc-collected coupled product indicated the presence of 0.20 ± 0.03 deuteron and no greater than 0.2 deuteron in the olefinic and saturated ring positions, respectively.

1-Chlorocycloheptene-2,7,7-d_3 and Phenyllithium. 1-Chlorocycloheptene-2,7,7-d_3 (5.1308 g, 0.03840 mole) and 110 ml of 1.03 *M* phenyllithium (0.113 mole) in ether were heated at 150 ± 10° for 1.3 hr. The reaction products included 1.83 g (35.8%; 20 CWA, 110°, 30 cc/min) of 1-chlorocycloheptene-2,7,7-d_3 and 0.97 g (14.6%; 20 CWA, 170°, 35 cc/min) of deuterated 1-phenylcycloheptene. Both compounds were isolated utilizing preparative glpc. The nmr and infrared spectra of the recovered chloride were virtually identical with those of the starting material. Proton nmr analysis of the deuterated 1-phenylcycloheptene indicated the presence of 0.17 ± 0.02 deuteron and 1.96 ± 0.12 deuterons in the olefinic and saturated ring positions, respectively.

***trans*-3-Chloro-2-pentene and Phenyllithium.** *trans*-3-Chloro-2-pentene (5.0482 g, 0.04828 mole) and 125 ml of 1.24 *M* phenyllithium (0.155 mole) in ether were heated at 150 ± 10° for 1.3 hr. Approximately one-half (2.25 g, 44.8%) of the starting chloride was recovered unreacted (10 CWA, 70°, 30 cc/min). Neither coupling products (*trans*- and *cis*-3-phenyl-2-pentene, *trans*- and *cis*-2-phenyl-2-pentene, 2-phenyl-1-pentene) nor acetylenic elimination products (1- and 2-pentyne) were observed (10 CWA, 70°, 135°, 30 cc/min).

1-Chlorocyclopentene, 1-Chlorocyclopentene-2,5,5-d_3, and Phenyllithium. A solution consisting of 6.0738 g (0.05926 mole) of 1-chlorocyclopentene, 2.3089 g (0.02188 mole) of 1-chlorocyclopentene-2,5,5-d_3, and 220 ml of 0.94 *M* phenyllithium (0.206 mole) in ether was heated at 150 ± 10° for 1.3 hr. Analysis of the products by glpc (20 CWA, 70°, 225°, 35 cc/min) showed that 2.97 g (35.3%) of unreacted olefinic chlorides and 2.47 g (21.2%) of substitution product were present. The chlorides were collected by glpc. Nmr analysis (biphenyl internal quantitative standard) indicated that 0.01428 mole of each reactant survived reaction. From this result a kinetic isotope effect, k_H/k_D, of 3.36 ± 0.40 was calculated[15] assuming simple competition. The nmr and infrared spectra of the substitution product were very similar to those for 1-phenylcyclopentene.

1-Chlorocyclohexene, 1-Chlorocyclohexene-2,6,6-d_3, and Phenyllithium. A solution consisting of 6.0233 g (0.05162 mole) of 1-chlorocyclohexene, 2.0236 g (0.01691 mole) of 1-chlorocyclohexene-2,6,6-d_3, and 180 ml of 1.00 *M* phenyllithium (0.180 mole) in ether was heated at 150 ± 10° for 1.3 hr. Analysis of the products by glpc (XEA, 90°, 160°, 35 cc/min) showed that 3.01 g (38.8%) of unreacted olefinic chlorides and 1.74 g (15.9%) of substitution product were present. The chlorides were collected by glpc. Nmr analysis (biphenyl internal quantitative standard) indicated that 0.01345 mole of 1-chlorocyclohexene and 0.01313 mole of 1-chlorocyclohexene-2,6,6-d_3 survived reaction. A k_H/k_D of 5.34 ± 0.40 was calculated[15] from these data. The nmr and infrared spectra of the substitution product were very similar to those for 1-phenylcyclohexene.

1-Chlorocycloheptene, 1-Chlorocycloheptene-2,7,7-d_3, and Phenyllithium. A solution consisting of 7.0284 g (0.05381 mole) of 1-chlorocycloheptene, 2.6302 g (0.01968 mole) of 1-chlorocycloheptene-2,7,7-d_3, and 230 ml of 0.74 *M* phenyllithium (0.170 mole) in ether was heated at 150 ± 10° for 1.3 hr. Analysis of the products by glpc (20 CWA, 110°, 170°, 35 cc/min) showed that 3.26 g (29.5%) of unreacted olefinic chlorides and 2.73 g (21.4%) of substitution product were present. The chlorides were collected by glpc. Nmr analysis (biphenyl internal standard) indicated that 0.00701 mole of 1-chlorocycloheptene and 0.01468 mole of 1-chlorocycloheptene-2,7,7-d_3 survived reaction. A k_H/k_D of 7.16 ± 0.40 was calculated[15] from these data. The nmr and infrared spectra of the substitution product were very similar to those for 1-phenylcycloheptene.

Possible Olefinic Products. A number of phenyl-substituted olefins were prepared from appropriate ketones by way of a two-step sequence. In the first, a tertiary phenylcarbinol was synthesized from the ketone (phenyllithium or phenylmagnesium bromide). The Grignard route was preferable owing to the fact that biphenyl, which was usually difficult to separate from the final product, invariably contaminated the phenyllithium preparations. When it was convenient, the phenylcarbinols were isolated and recrystallized. The second step consisted of formic acid dehydration.[6]

2-Methyl-1-phenylcyclopentene and 3-methyl-2-phenylcyclopentene[30] were prepared from 2-methylcyclopentanone. The two olefins could not be conveniently separated by preparative glpc and were isolated as a mixture (XEP, 205°, 200 cc/min). The mixture possessed important infrared absorption bands at ~1650, ~1621, 1597, and 1571 cm^{-1}. The C=C stretching bands overlapped and were difficult to assign precisely. The nmr spectrum consisted of complex absorption from 7.6 to 7.0 (5.0 protons, assigned), complex absorption from 6.07 to 5.87 (0.29 proton), complex absorption from 2.9 to 1.5 (4.94 protons) which included a multiplet associated with the methyl groups of 2-methyl-1-phenylcyclopentene at 1.80, and a doublet (7 cps, 0.089 proton) at 1.07.

3-Methyl-1-phenylcyclopentene and 4-methyl-1-phenylcyclopentene were prepared from 3-methylcyclopentanone. The mixture of olefins (XEP, 205°, 200 cc/min) possessed important infrared absorption bands at 1623, 1597, and 1572 cm^{-1}. The nmr spectrum of the mixture consisted of complex absorption from 7.4 to 6.8 (5.0 protons, assigned), complex absorption from 5.95 to 5.78 (0.93 proton), complex absorption from 3.0 to 1.1 (4.9 protons), and a doublet (6.5 cps) at 1.05 (2.9 protons).

2-Methyl-1-phenylcyclohexene and 3-methyl-2-phenylcyclohexene[31] were prepared from 2-methylcyclohexanone and separated employing glpc (XEP, 205°, 200 ml/min).

3-Methyl-1-phenylcyclohexene and 4-methyl-2-phenylcyclohexene[32] were prepared from 3-methylcyclohexanone. The mixture of of isomers possessed important infrared absorption bands at ~1645, 1597, and 1645 cm^{-1} The nmr spectrum of the isomers consisted of complex absorption at 7.6–6.9 (5.0 protons, assigned), complex absorption at 6.15–5.92 (1.00 proton), and complex absorption at 2.6–0.9 (10.2 protons), which included two overlapping doublets (5–7 cps) centered near 1.05.

1-Phenylcyclopentene, 1-phenylcyclohexene, 1-phenylcycloheptene, *trans*- and *cis*-3-phenyl-2-pentene, *trans*- and *cis*-2-phenyl-2-pentene, and 2-phenyl-1-pentene were also prepared in high purity from appropriate ketones.

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1-Chlorocyclohexene-2,6,6-d_3 and Phenyllithium. 1-Chlorocyclohexene-2,6,6-d_3[6] (4.5663 g, 0.03815 mole) and 100 ml of 1.00 *M* phenyllithium (0.100 mole) in ether were heated at 150 ± 10° for 1.3 hr. The reaction products included 2.13 g (46.6%; XEA, 90°, 35 cc/min) of 1-chlorocyclohexene-2,6,6-d_3 and 0.79 g (12.5%) of deuterated 1-phenylcyclohexene. Both compounds were isolated utilizing preparative glpc. The nmr and infrared spectra of the recovered chloride were virtually identical with those of the starting material. Proton nmr analysis of the deuterated 1-phenylcyclohexene indicated the presence of 0.82 ± 0.09 deuteron and 1.93 ± 0.11 deuterons in the olefinic and saturated ring positions, respectively.

Proton Transfers in Dipolar Aprotic Solvents. III. Transfers from Triphenylmethane in Dimethyl Sulfoxide Solution[1,2]

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Abstract: The reactions of triphenylmethane with *t*-butoxide, *n*-propoxide, and dimsyl ions in dimethyl sulfoxide solution have been studied. Triphenylmethane reacts with dimsyl ion and *n*-propoxide ion to form trityl anion with second-order rate constants of 8×10^3 and 6×10^3 M^{-1} sec^{-1}, respectively. The reaction of triphenylmethane with *t*-butoxide ion is too slow to measure under our reaction conditions, and an upper limit of 8×10^2 M^{-1} sec^{-1} is set on the rate constant for this reaction. Equilibrium constants for the reactions of triphenylmethane with dimsyl ion, *t*-butoxide ion, and *n*-propoxide ion are 1.6×10^4, 0.5, and 0.1, respectively.

As part of a continuing study of solvent effects on the rates of proton transfer reactions, we have measured the rates and equilibrium constants for the reactions of triphenylmethane with dimsylcesium, potassium *t*-butoxide, and potassium *n*-propoxide in dimethyl sulfoxide solution. Since the results obtained are pertinent to a number of recently reported studies of rates and equilibria of carbon acids,[3] we wish to report these data now. Several corrections are made to a preliminary report of this work.[4]

Experimental Section

All materials were purified, stored, and handled under an atmosphere of purified argon.[5]

Materials. Dimethyl sulfoxide was purified by the method previously described,[5] and was found to contain less than 5×10^{-6} *M* acidic and basic impurities, and less than 20 ppm of water.

Dimsylcesium solutions of *ca.* 0.3 *M* were prepared from cesium amide as previously described.[5] Less concentrated solutions were prepared by dilution. The ultraviolet spectrum of a 2.4×10^{-2} *M* solution of cesium dimsyl in a 0.1-mm cell showed an absorption shoulder at 260 mμ (ϵ 1.5×10^3 M^{-1} cm^{-1}), and no peaks or shoulders at longer wavelengths. The 60-Mc nmr spectrum of a 0.24 *M* solution showed a single sharp peak for the solvent and *no* other visible bands within 800 cps on either side of the solvent peak. Any band with an intensity of as much as 0.5% of that of the solvent would have been seen. The infrared spectrum of a 0.24 *M* solution of dimsylcesium *vs.* pure dimethyl sulfoxide showed a single band at 840–850 cm^{-1} ($\epsilon \simeq 1.2 \times 10^2$ M^{-1} cm^{-1}) which we believe to be due to the S–O stretch of the dimsyl ion.

Potassium *t*-butoxide (MSA Research Corp.) was twice sublimed under vacuum at *ca.* 100° prior to use.

Potassium *n*-propoxide was prepared by reaction of metallic potassium with dry deoxygenated *n*-propyl alcohol, followed by removal of excess *n*-propyl alcohol under vacuum. The resulting product was dried under vacuum at *ca.* 100° for 3 hr. Titration of a weighed sample of the alkoxide with aqueous standard acid indicated a purity of better than 99.5%.

Triphenylmethane was recrystallized from ethanol and dried under vacuum prior to use.

A sample of triphenylmethane-d_1 was kindly supplied by Professor P. T. Lansbury. Infrared analysis of the material showed greater than 90% isotopic purity.

Apparatus. Equilibrium measurements were carried out on a Cary Model 14 spectrophotometer fitted with the mixing cell apparatus diagrammed in Figure 1, and further described below.

Kinetic measurements were carried out on a small-scale stop-flow apparatus which we have previously described.[6]

Equilibrium Measurements. Solutions of triphenylmethane (the concentrations of triphenylmethane in the various measurements ranged from 5×10^{-6} *M* to *ca.* 10^{-4} *M* in each determination) were added incrementally by means of a micrometer syringe, whose tip extended into the bulb of the apparatus shown in Figure 1, to 10.0 ml of the base solutions contained in the mixing cell. The solutions were mixed after each addition by simply tipping the cell back and forth several times. Care was taken that the solutions did not contact the rubber serum cap through which the syringe was inserted.

Plots of absorbance at 495 mμ, the wavelength of maximum absorption of the trityl anion, *vs.* concentration of triphenylmethane added gave straight lines whose slopes are the apparent extinction coefficients, ϵ'. Several experiments utilizing *ca.* 10^{-1} *M* solutions of dimsylcesium gave the true extinction coefficient of the trityl anion, ϵ, as 3.12×10^4 M^{-1} cm^{-1}. At lower concentrations of dimsyl anion, the observed apparent extinction coefficients can be used to calculate the ratio of trityl anion to triphenylmethane concentrations in the solution by eq 1.

$$(\mathrm{Ar_3C^-})/(\mathrm{Ar_3CH}) = \epsilon'/(\epsilon - \epsilon') \qquad (1)$$

This technique of measurement is necessary because of small amounts of impurities present which react with either the trityl anion or triphenylmethane. The fact that non-zero intercepts are obtained in the plots of absorbance *vs.* concentration show the presence of such impurities. One such plot is shown in Figure 2.

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