

Metalation of Cyclopentene and Cyclohexene. The Effects of Ring Size and Alkali Metal Cation

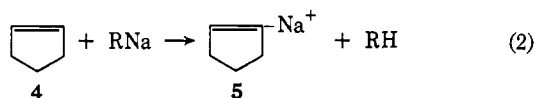
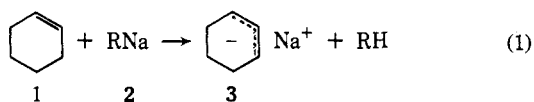
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Abstract: Metalation of cyclopentene with *n*-butylsodium has been shown to produce 1-sodiocyclopentene. With *n*-butylpotassium, both 1-potassio and 3-potassio derivatives are realized. Metalation of cyclohexene with either *n*-butylsodium or *n*-butylpotassium resulted in reaction at the allylic position to produce the 3-substituted organometallic. Competitive metalation of cyclopentene-cyclohexene mixtures with *n*-butylsodium gave exclusively 1-sodiocyclopentene at short reaction times. Similar competitive metalation with *n*-butylpotassium produced 1- and 3-potassiocyclopentenes as well as 3-potassiocyclohexene. Alternately synthesized 1-potassiocyclopentene underwent reaction slowly with excess olefin to produce 3-potassiocyclopentene. The vinylsodio compound was stable to the reaction conditions. These results are discussed in terms of kinetic *vs.* thermodynamic processes, hybridization changes, ring strain, and extent of electron delocalization with change in alkali metal.

Recent studies on hydrocarbon metalation indicate that both ground-state hybridization effects and resonance stabilization operate to determine the initial site of metalation.¹⁻³ In those systems wherein kinetic *vs.* thermodynamic processes have been considered, it appears that rapid initial reaction between unsaturated hydrocarbon and saturated metalating agent is followed by slower rearrangements⁴ involving *trans* metalation. The data also suggest that metalation reactions using alkylpotassium compounds differ from alkylsodium reactions in that the more ionic potassium reagents favor initial reaction at positions leading to resonance-stabilized organometallics. In view of these observations, the contrasting results reported in metalation of cyclopentene and cyclohexene became of especial interest.

Morton and Finnegan⁵ have shown that cyclohexene affords the allyl carbanionic species upon reaction with amylsodium (eq 1) while cyclopentene gives a vinyl organometallic derivative (eq 2). The reaction of cyclopentene has been considered to be analogous to metalation of norbornene, wherein reaction at the



vinyl position is also observed,⁶ in that inhibition of reaction at the allylic site has been invoked to ration-

alize both results.⁶ In the case of norbornene, resonance stabilization of the bridgehead anionic species would be expected to be of little importance; therefore metalation at the vinylic site is not surprising. Finnegan⁶ has suggested that metalation of cyclopentene at an allylic position is retarded by the increased strain which would be encountered upon introduction of a third trigonal carbon atom in the five-membered ring. This factor then could account for the occurrence of exclusive vinylic metalation.

Since this work was reported before the recognition of kinetic *vs.* thermodynamic processes, we have extended these studies to include comparative metalations with alkylsodium and alkylpotassium reagents as well as competitive reactions of cyclopentene and cyclohexene.

Results

Metalation of Cyclopentene. The present results completely confirm the earlier report of Morton and Finnegan⁵ that the reaction of cyclopentene with a saturated alkylsodium compound, in this case *n*-butylsodium, results in the formation of 1-sodiocyclopentene as the predominant product. Portions of a reaction mixture of cyclopentene and *n*-butylsodium in a molar ratio of 4:1, respectively (see Experimental Section), were removed after 1 day, 2 days, and 1 week. These portions were separately carbonated, esterified, and analyzed by gas-liquid partition chromatography (glpc) to show the presence of only methyl 1-cyclopentenylcarboxylate as an olefin-derived product.

In contrast to these results, similar metalation of cyclopentene with *n*-butylpotassium gave the data recorded in Table I. It is at once apparent that allylic metalation becomes a factor in the potassium system.

Metalation of Cyclohexene. As was reported by Morton and Finnegan⁵ the reaction of cyclohexene with alkylsodium reagents results very predominantly in allylic metalation. A minimum of 99% of the olefin-derived product was accounted for by methyl 2-cyclohexenylcarboxylate using *n*-butylsodium followed by carbonation and esterification of the metalation mixture after 3 days. It was apparent that metalation of cyclohexene by *n*-butylsodium occurred much less readily than did metalation of cyclopentene. Thus, after a 4-hr metal-

(1) (a) C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 4174 (1966); (b) C. D. Broaddus, *J. Org. Chem.*, **29**, 2689 (1964); (c) C. D. Broaddus, T. J. Logan, and T. J. Flaunt, *ibid.*, **28**, 1174 (1963).

(2) (a) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *J. Am. Chem. Soc.*, **85**, 3984 (1963); (b) R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *ibid.*, **84**, 4971 (1962); (c) R. A. Benkeser and T. V. Liston, *ibid.*, **82**, 3221 (1960).

(3) (a) D. Bryce-Smith, *J. Chem. Soc.*, 5983 (1963); (b) D. Bryce-Smith, V. Gold, and D. P. N. Satchell, *ibid.*, 2743 (1954).

(4) Previous articles in this area^{1,2} have referred to these processes as rearrangement reactions, and this terminology will be retained in the present discussion for the sake of clarity although isomerization of the anionic species would be more proper.

(5) A. A. Morton and R. A. Finnegan, *J. Polymer Sci.*, **38**, 19 (1959).

(6) R. A. Finnegan and R. S. McNees, *Chem. Ind. (London)*, 1450 (1961).

Table I. Metalation of Cyclopentene with *n*-Butylpotassium^a

Time, hr	Methyl 1-cyclopentenyl-carboxylate	Methyl 2-cyclopentenyl-carboxylate
0.5	82	18
1.0	79	21
2.0	76	24
3.0	75	25
50.0	63	37

^a A 4:1 molar ratio of cyclopentene to *n*-butylpotassium, based on the amount of *n*-butyl chloride used in formation of the metalating agent, was present in these reactions.

ation period carbonation of a 4:1 mixture of cyclohexene and *n*-butylsodium gave essentially no cyclic acidic product, whereas, under the same conditions, easily distinguishable amounts of methyl 1-cyclopentenylcarboxylate were realized from cyclopentene following esterification. These observations led to the competitive experiments described below. Metalation of cyclohexene with *n*-butylpotassium also gave only allylic metalation. Portions of a reaction mixture were carbonated after 2.5 hr and 2.5 days. Esterification with diazomethane and glpc analysis showed only methyl 2-cyclohexenylcarboxylate as a cyclohexene-derived product.⁷ That there was no methyl 1-cyclohexenyl- or methyl 3-cyclohexenylcarboxylate present was shown by comparing glpc retention times and nmr spectra of the product to authentic samples.⁸

Competitive Metalation of Cyclopentene and Cyclohexene. Portions were removed from a metalation mixture consisting of cyclohexene (0.2 mole), cyclopentene (0.2 mole), and *n*-butylsodium (0.1 mole)⁹ in octane after stirring for 3 hr and 6 hr. Carbonation and esterification provided a mixture of methyl valerate and methyl 1-cyclopentenylcarboxylate with no detectable amount of product arising from cyclohexene. At long reaction times (46 hr) trace amounts of methyl 2-cyclohexenylcarboxylate were detected.

A similar reaction in which *n*-butylpotassium was substituted for *n*-butylsodium gave the results recorded in Table II.

Alternate Synthesis and Stability of Vinyl Anionic Intermediates. Addition of 1-bromocyclopentene to a sodium sand in octane provided 1-sodiocyclopentene as determined by carbonation of a portion of the reaction mixture and identification of the acidic product (see Experimental Section). A 4 *M* excess of cyclopentene was added to the remaining metalation mixture and stirring was continued overnight. Carbonation and product identification after this time interval showed only the presence of methyl 1-cyclopentenylcarboxylate as a product derived from cyclopentene. It is then apparent that the vinyl anionic species produced in this manner is stable to these reaction conditions for the time intervals involved.

Formation of 1-potassiocyclopentene occurred in a manner analogous to the sodium case using either 1-bromocyclopentene or 1-chlorocyclopentene and potas-

(7) It is apparent that metalation by *n*-butylpotassium occurs more rapidly than by *n*-butylsodium, in agreement with earlier work [H. Gilman and J. W. Morton, Jr., *Org. Reactions*, 8, 283 (1954)].

(8) Samples of methyl 1-cyclohexenyl- and methyl 3-cyclohexenylcarboxylate were kindly supplied by Dr. R. A. Damico of these laboratories.

(9) Based on the amount of *n*-butyl chloride used in reaction with the appropriate metal.

Table II. Competitive Metalation of Cyclohexene and Cyclopentene with *n*-Butylpotassium

Time, hr ^a	Methyl 1-cyclopentenyl-carboxylate	Methyl 2-cyclopentenyl-carboxylate	Methyl 2-cyclohexenyl-carboxylate
0.5	49	11	40
1	44	14	42
3 ^b	34 (34)	15 (14)	51 (52)
5	30	13	57
7	24	12	64
23	8	9	83

^a Elapsed time after addition of the olefins to the *n*-butylpotassium. ^b These data were obtained from two separate runs with portions removed from both mixtures after a 3-hr interval. The excellent agreement, shown in parentheses, at the common time interval could be in large part coincidental, and only the general trends of the data are considered significant.

sium sand. Addition of a 4 *M* excess of cyclopentene and work-up of portions of the reaction mixture showed very little formation of the allyl anionic species during the first 3 hr following the olefin addition. After 23 hr, carbonation and product identification (glpc) of methyl esters indicated a mixture consisting of 87% methyl 1-cyclopentenyl- and 13% methyl 2-cyclopentenylcarboxylates. In an analogous experiment, wherein a 4 *M* excess of cyclohexene was added to 1-potassiocyclopentene, the product was analyzed 23 hr after addition of the excess olefin and was found to be a mixture of 80% methyl 1-cyclopentenyl- and 20% methyl 2-cyclohexenylcarboxylates. It is then clear that some rearrangement of 1-potassiocyclopentene occurs in the presence of either cyclopentene or cyclohexene, but that the process is relatively slow.

The vinyl potassio derivative of cyclohexene was produced in the same manner and excess cyclohexene added to the reaction mixture. Carbonation of aliquots removed after 45 min and 2.5 hr gave only methyl 1-cyclohexenylcarboxylate as shown by glpc analysis of the esterified product.

It should be emphasized at this point that although both the metalation studies and alternate synthesis of vinylic intermediates indicate that rearrangement to resonance-stabilized organometallics is relatively slow, a slight inconsistency emerges from the data. Thus, from the data of Table II, it appears that 1-potassiocyclopentene is reduced from ~50% of the organometallic mixture to ~10% in the presence of excess cyclohexene after 23 hr, while alternate synthesis of 1-potassiocyclopentene followed by addition of cyclohexene shows a reduction from 100 to 80% of this vinyl potassium compound after the same time interval. Since all of these reaction systems are heterogeneous, better agreement between the rates of rearrangement might not be expected.

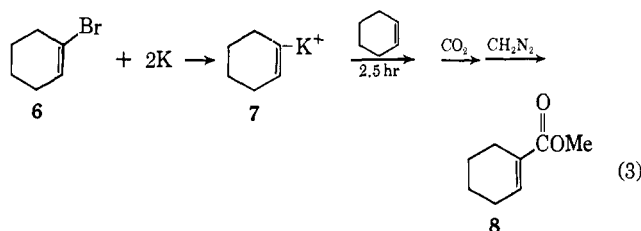
In the discussion that follows, carbonation products are assumed to characterize the organometallic species present in the various reaction mixtures. If double-bond isomerization occurred during work-up, the conclusions would, of course, be invalid. However, several observations rule against isomerization being an important factor under these conditions. For example, it has been reported¹⁰ that the equilibrium distribution of 2-carboxycyclohexene and 1-carboxycyclohexene is

(10) E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, 258 (1935).

5:95, respectively. The present synthesis of 1-sodio-cyclohexene followed by carbonation and the usual work-up procedures gave only methyl 1-cyclohexenyl-carboxylate. Since only methyl 2-cyclohexenyl-carboxylate was realized from metalation of cyclohexene followed by carbonation and esterification, it is obvious that isomerization did not occur during work-up of these reaction products.¹¹ Similarly, 1-potassiumcyclopentene, from the reaction of 1-bromocyclopentene and potassium metal, gave only methyl 1-cyclopentenyl-carboxylate while metalation of cyclopentene with *n*-butylpotassium yielded easily distinguishable amounts of both methyl 1-cyclopentenyl- and methyl 2-cyclopentenylcarboxylates. If isomerization of the unsaturated acids were a rapid process, under the work-up conditions, the same distribution of unsaturated cyclic acids would be expected.

Discussion

The results obtained from these studies are consistent with and support the general concepts outlined in our earlier work.¹ Thus, with both cyclopentene and cyclohexene, using either *n*-butylsodium or *n*-butylpotassium, the data indicate that relatively rapid initial metalation processes are followed by slower rearrangement reactions. In the case of cyclopentene and *n*-butylsodium, the initial metalation reaction produces 1-sodiocyclopentene and there is no evidence for rearrangement to the allyl derivative even when the reaction is conducted for 1 week in the presence of excess cyclopentene. Neither is there evidence for rearrangement upon generation of the vinyl derivative from the corresponding bromo compound followed by addition of excess cyclopentene. This system then represents a case of selective metalation at a vinyl position.⁵ Next consider the reaction of cyclohexene with *n*-butylpotassium. Here carbonation of the reaction mixture after 2.5 hr gave an acidic metalation product which was exclusively attributable to proton abstraction at the allylic position. Generation of the vinyl potassio derivative, from 1-bromocyclohexene and potassium sand, and addition of excess cyclohexene resulted in only methyl 1-cyclohexenylcarboxylate upon carbonation and esterification after a 2.5-hr reaction period (reaction 3). These data then exclude rapid reaction at a vinyl position followed by rearrangement during the metalation process and suggest that this system is one wherein initial metalation occurs at the allylic position.¹²



(11) The equilibrium distribution of methyl cyclohexenylcarboxylates has been shown to be 87% methyl 1-cyclohexenyl-, 4% methyl 2-cyclohexenyl-, and 8% methyl 3-cyclohexenylcarboxylates [R. A. Damico, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967].

(12) Metalation of cyclohexene with *n*-butylsodium appears to fit the same scheme in that only allylic metalation has been observed; however, 1-sodiocyclohexene has not been shown to be stable to the reaction conditions.

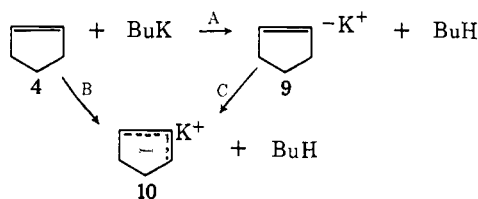


Figure 1.

Another generality which arose from the earlier work concerns the relative facility for reaction at sp^2 C-H positions *vs.* potentially resonance-stabilized sp^3 C-H sites with change in metalating agent from alkylsodium to alkylpotassium. These earlier studies and the work of others^{2,3} indicated that the use of an alkylpotassium compound favors reaction at a resonance-stabilized position relative to the use of alkylsodium reagents. Thus, comparative metalations of 1-olefins,^{1b} toluene,^{1a} ethylbenzene,² and cumene³ are all consistent with this proposal. Comparison of the data obtained from metalation of cyclopentene with *n*-butylsodium and *n*-butylpotassium, described in the Results, also supports this view.

As shown in eq 2, metalation of cyclopentene with *n*-butylsodium follows the course described by Morton and Finnegan⁵ and appears to be a simple vinyl proton abstraction. The reaction of cyclopentene with *n*-butylpotassium is more complicated. From the data recorded in Table I it appears that initial metalation of cyclopentene involves competitive reaction at allyl and vinyl sites with vinylic abstraction being the favored process (Figure 1), *i.e.*, $A > B$. Thus, plotting the ratio of products derived from 9 and 10 against time indicates that the initial reaction occurs about four to five times more readily at the vinyl than at the allyl position. Both the relatively slow change in the composition of acidic product and the stability of alternately synthesized 1-potassiumcyclopentene show that rearrangement to the allyl isomer occurs slowly relative to the initial metalation process, *i.e.*, $A > B > C$ in Figure 1. These observations then support the earlier comparisons of alkylsodium to alkylpotassium metalation reactions. Thus, it is apparent that reaction at the allylic position is favored by the use of an organopotassium metalating agent relative to the reaction with organosodium compounds. This phenomenon has been rationalized by attributing greater importance to electron delocalization in the more ionic organopotassium system.¹ That is, in a competitive situation wherein reaction occurs at both resonance-stabilized and nonstabilized sites, greater ionic character is thought to favor reaction at the resonance-stabilized position by an increase in the facility of electron delocalization in the transition state for proton abstraction. While these considerations indicate that metalation of cyclopentene concurs with the general observations in metalation of hydrocarbons, they lend no insight into the question of why vinylic metalation increases in importance in the five-membered olefinic system. This question is discussed below.

Metalation of cyclohexene with both *n*-butylsodium and *n*-butylpotassium gave very predominantly the allyl derivative. Allylic metalation has also been observed in the reaction of *cis*-cyclooctene with *n*-

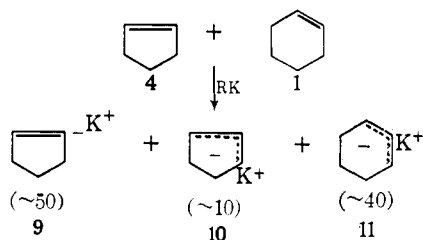


Figure 2.

butylpotassium.¹³ These examples correspond to the metalation of acyclic olefins in that reaction is found to be quite slow (not observed) at vinyl positions adjacent to alkyl substituents.^{1b,c} It is then the cyclopentene system which requires further consideration.

As mentioned in the introductory section, Finnegan⁶ made the reasonable proposal that reaction at the allylic position is retarded in the cyclopentene case by the strain which would be encountered upon introducing a third trigonal carbon atom into the five-membered system. However, recent work on rates of base-catalyzed exchange¹⁴ and bromination of cyclic ketones¹⁵ as well as rates of isomerization of exocyclic olefins¹⁶ indicates that five-membered ring systems undergo more rapid proton loss than do the corresponding six-membered compounds. It has been suggested that increased *s* character in the C–H bonds of the more highly strained five-membered ring systems accounts for the increased ease of proton removal.^{14,16} To gain some insight into the operation of these factors during metalation, competitive reactions using mixtures of cyclopentene and cyclohexene were conducted.

Carbonation of a metalation mixture composed of a 1:1 *M* ratio of cyclopentene to cyclohexene admixed with *n*-butylsodium after 6 hr provided methyl 1-cyclopentenylcarboxylate as the predominant product following esterification. It is immediately obvious from this result that an explanation of cyclopentene metalation, as compared to cyclohexene, based solely on inhibition of reaction at the allylic position is not tenable. Thus, the observation requires increased reactivity of the C₅ vinyl site as compared to both the allylic positions of cyclopentene and the allylic positions of cyclohexene, and it is therefore not reasonable to propose that some factor inhibiting reaction in the C₅ allyl case is solely responsible for the metalation results.

This enhanced reactivity does appear rational on the basis of increased *s* character in the C–H bond involved. As discussed above and in earlier work,¹ resonance stabilization does not play an overwhelming role in metalation systems involving organosodium compounds. For example, it appears clear that the initial metalation of cumene by amylsodium occurs at ring positions to the virtual exclusion of the potentially resonance-stabilized benzylic site.² In the present reaction the vinylic site of cyclopentene undergoes metalation by *n*-butylsodium more rapidly than the allylic positions of either olefin. If the olefinic C–H

bonds of cyclopentene do indeed have relatively high *s* character, as may be indicated by the reported ¹³C–H coupling constants,¹⁷ then rapid reaction at this position relative to the allylic positions might be anticipated.

Competitive metalation of cyclopentene and cyclohexene with *n*-butylpotassium is also quite revealing. As shown in Table II the data indicate that at short reaction times simple competitive metalation of the two olefinic systems is observed, *i.e.*, again the initial metalation processes involving *n*-butylpotassium are rapid compared to any subsequent rearrangement processes. This conclusion is supported by the observation that the ratio of methyl 1-cyclopentenyl- to methyl 2-cyclopentenylcarboxylates after a 0.5-hr metalation period is essentially the same in the competitive experiment (Table II) as that observed in the metalation of cyclopentene (Table I). Also, it can be seen from Table II that while the composition of the acid mixture does change with time, the change is a rather slow smooth process. It then appears safe to assume that the initial metalation involves competitive reactions to produce the three anionic species in approximately the relative yields given in Figure 2. Two points stand out in these data. First, the over-all rate of metalation of cyclopentene and cyclohexene are roughly comparable, and second, the facility for metalation at the three types of positions are in the order C₅ vinylic ≈ C₆ allylic > C₅ allylic.

The fact that the over-all rates of metalation of these two olefinic systems approach equality when treated with *n*-butylpotassium whereas cyclopentene reacts more rapidly than cyclohexene with *n*-butylsodium is most easily understood on the basis that resonance stabilization plays a more important role in the case of the more ionic potassium base. As noted above allylic intermediates are not observed at short reaction times in the competitive metalation with alkylsodium compounds, but make up approximately 50% of the initial metalation mixture in the case of butylpotassium. The activation energies for formation of the two types of species are then more nearly equal in the latter case and it seems reasonable to propose an increased effectiveness of resonance stabilization to account for the results.

Perhaps the most noteworthy observation to make concerning the order C₅ vinylic ≈ C₆ allylic > C₅ allylic is the fact that the C₆ allylic product is formed to a greater extent than is the C₅ allylic product. Since any increased *s* character, with reduction in ring size, would favor faster reaction by cyclopentene, it appears that some factor retarding reaction at the allylic positions of cyclopentene is operative. Finnegan's proposal of increased strain would account for this observation. It should be pointed out that the previous studies^{14–16} of effect of ring size on rates of proton removal were performed in systems in which the number of nominally sp² carbon atoms changed from one to two upon proton loss,¹⁸ whereas the present reactions involve a transition from two to three sp² carbon atoms.

(13) W. F. Erman and H. C. Kretschmar, *J. Am. Chem. Soc.*, **89**, 3842 (1967).

(14) H. Schechter, M. J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *ibid.*, **84**, 2905 (1962).

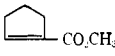
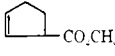
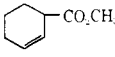
(15) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

(16) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 51, gives a discussion of this factor.

(17) The vinyl ¹³C–H coupling constants are reported [P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963)] to be cyclopentene, 160 and cyclohexene, 157 which is directionally correct for greater *s* character in the cyclopentene system.

(18) The effect of ring size on rates of nitrocyane neutralizations has also been reported (ref 16, p 51) to show increased reactivity of cyclopentyl relative to cyclohexyl systems.

Table III. Characterization of Unsaturated Esters

Compd	τ	Multiplicity	Rel area	Formula	C, %		H, %	
					Calcd	Found	Calcd	Found
	3.40	Triplet	1	C ₇ H ₁₀ O ₂	66.67	66.46	7.94	7.92
	6.42	Singlet	3					
	7.54	Multiplet	4					
	8.10	Multiplet	2					
	4.32	Multiplet	2	C ₇ H ₁₀ O ₂	66.67	66.62	7.94	8.00
	6.48	Singlet	3					
	6.60	Multiplet	1					
	7.80	Multiplet	4					
	4.28	Singlet	2	C ₈ H ₁₂ O ₂	68.57	68.51	8.57	8.60
	6.38	Singlet	3					
	6.99	Multiplet	1					
	8.15	Multiplet	6					

The influence of increased acidity of vinylic protons in cyclopentene is still evident in the data of Table II in the large amounts of methyl 1-cyclopentenylcarboxylate formed after short reaction periods. The fact that the relative yield of this material decreases markedly with time, although rather slowly, corroborates the operation of kinetic *vs.* thermodynamic processes during metalation reactions.² There are several earlier examples of metalation processes in which reaction at a C-H bond high in s character is kinetically favored over a potentially resonance-stabilized site.^{1,2} The most straightforward conclusion to draw from these results is that the position of metalation is *not* controlled by the thermodynamic acidity of the hydrocarbon. Contrast this with the many isotopic exchange studies in which reaction occurs exclusively at the resonance-stabilized position.¹⁹ It seems reasonable to suggest that in metalation systems, which involve very strongly basic reagents in nonsolvating media, the ground-state hybridizations of the C-H bonds in question are a more important factor in determining kinetic acidity. Thus, it is well known that sp² C-H bonds are more acidic than sp³ C-H positions in the absence of resonance effects. Since metalation is observed at sp² C-H sites with systems possessing potentially resonance-stabilized sp³ C-H positions, it follows that resonance stabilization is not as effective in these reactions as it is in base-catalyzed isotopic exchange.

Experimental Section

Materials. Cyclopentene was obtained from the Aldrich Chemical Co. and Matheson Coleman and Bell. Cyclohexene, cyclopentanone, valeric acid, *n*-butyl chloride, and *n*-octane were purchased from Matheson Coleman and Bell. Phosphorus pentachloride came from the Baker Co., while *N*-nitroso-*N*-methylurea was obtained from the Aldrich Chemical Co. Methyl valerate was prepared by the esterification of valeric acid.

Analyses. Gas-liquid partition chromatographic analyses were performed on an F & M Model 700 instrument using 6-ft columns. The analytical results were obtained on a 0.125-in. diameter column packed with 10% SE-30 on 80-100 mesh Diatoport S while the collection of isomeric esters was accomplished from a 0.25-in. column containing 10% Apiezon L on 60-80 mesh Chromasorb W, acid washed and dimethyldichlorosilane treated. Compositions of the products were determined from the relative areas obtained by multiplying the peak height by the width at half-height.

Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer.

(19) Reference 16, Chapter 1.

Nuclear magnetic resonance (nmr) spectra were obtained on a Varian HA-100 spectrometer using tetramethylsilane as the internal standard from which shifts in τ units refer.

Elemental analyses were carried out by Spang Laboratories, Ann Arbor, Mich.

Metalating Agents. *n*-Butylsodium and *n*-butylpotassium were prepared by the addition of *n*-butyl chloride to a previously prepared dispersion of the respective metal in *n*-octane at 0°. Previous results obtained under these same conditions established that yields of metalating agent (as measured by the acidic product formed upon carbonation) varied from 60 to 70% for *n*-butylsodium and from 40 to 50% for *n*-butylpotassium.¹ In this work the presence of valeric acid (as shown by infrared and glpc comparison of the esterified product with authentic methyl valerate) was taken as proof that *n*-butylsodium and *n*-butylpotassium had been formed.

Characterization of Acidic Products. Esterification of the crude mixtures of acidic products was accomplished by addition of diazomethane in ether.²¹ The methyl esters of the isomeric acids were characterized by nmr and elemental analysis. The results are shown in Table III.

Metalation of Olefins. The metalation of cyclopentene by an *n*-butylpotassium dispersion is given as a typical example of this type of reaction. An *n*-butylpotassium dispersion was generated in the usual manner from 7.8 g (0.2 mole) of potassium sand and 9.2 g (0.1 mole) of *n*-butyl chloride in 175 ml of *n*-octane. To this mixture, rapidly stirring at room temperature, was added 27.2 g (0.4 mole) of cyclopentene. After stirring for 3 hr, an aliquot was removed for carbonation and the remainder transferred to a single-necked, round-bottomed flask which was sealed to exclude moisture. A heavy flow of argon over the surface of the liquid was maintained during the transfer. The reaction mixture was then stirred magnetically overnight under argon before carbonation with Dry Ice. After esterification, the products were analyzed by glpc (see Table I for product ratios). Pure samples of both isomeric cyclopentenyl esters were collected from the glpc and submitted for nmr and elemental analysis. The nmr spectra indicate that the compound with the shortest glpc retention time is the β,γ -cyclopentenyl ester. The results are shown in Table III.

A typical run in which the entire metalation mixture was carbonated after 20 hr gave a 44% yield, based on *n*-butyl chloride, of crude acid product.

1-Bromocyclopentene was prepared by the method of Maitte²² from cyclopentene. The product was obtained in an over-all yield of 22% as a clear liquid, bp 69° (100 mm) (lit.²² bp 24° (13 mm)). The nmr spectrum was consistent with the proposed product, exhibiting a broad peak at τ 4.30 and a series of three multiplets between τ 7.40 and 8.30, relative areas 1:6.

1-Bromocyclohexene was prepared from cyclohexene by the method of Maitte²² in a total yield of 10%, bp 52° (14 mm) (lit.²² bp 54° (17 mm)). The nmr spectrum showed a multiplet at τ 4.15 and three multiplets between τ 7.60 and 8.60 with an area ratio of 1:8, which would be expected for the desired product.

(20) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

(21) F. G. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 165.

(22) P. Maitte, *Bull. Soc. Chim. France*, 499 (1959).

1-Chlorocyclopentene was prepared from cyclopentanone and phosphorus pentachloride following the procedure reported by Mousseron and Jacquier.²³ The product was obtained in a 28% yield as a clear colorless liquid, bp 49° (100 mm), n_D^{25} 1.4632 (lit.²³ bp 115° (760 mm), n_D^{25} 1.4637). The nmr spectrum was consistent with the desired structure, exhibiting a multiplet at τ 4.43 and two multiplets at τ 7.60 and 7.98, relative areas 1:4:2.

Formation of Vinyl Sodio and Potassio Compounds. The preparation of 1-sodiocyclopentene is given as a typical example of this type of reaction. A dispersion of sodium (4.6 g, 0.2 g-atom) was

(23) M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 648 (1950).

formed in the usual manner and cooled to 0°. 1-Bromocyclopentene (14.7 g, 0.1 mole) was slowly dripped into the rapidly stirring mixture during about 30 min, and the resulting mixture was allowed to warm to room temperature. After stirring for 30 min, one-third the volume of the dispersion was removed and carbonated, giving 2.1 g (~57%) of crude cyclopentene-1-carboxylic acid (see Table III).

Competition Experiments. The conditions used for competition experiments were the same as in the normal metalation reactions, with the total molar quantity of olefin present remaining the same and being equally divided between the two olefins used.

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Free Radicals in Thermal and Photochemical Oxidative Decarboxylations with Lead(IV)

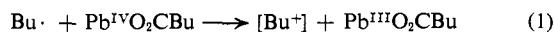
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Abstract: The rates and products of decarboxylation of acids by Pb(IV) acetate differ widely according to their structure. Tertiary and α -aralkyl acids are readily decarboxylated and afford alkene and ester as products of oxidation in high yields, in contrast to primary and secondary aliphatic acids. Effect of inhibitors and scavengers and detection of radicals by electron spin resonance indicate that the mechanism of decarboxylation is the same for all these classes of acids. A free-radical chain sequence (eq 1 and 2) is involved. The relative rates of oxidation of alkyl radicals by Pb(IV) largely determine the distribution of products, being fastest with tertiary and related radicals. The photochemical reaction at 30° is equivalent to a thermal reaction at 80° and in most cases affords better yields of the same products. High quantum yields indicate an efficient chain reaction in the decarboxylation of tertiary acids.

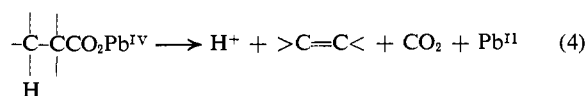
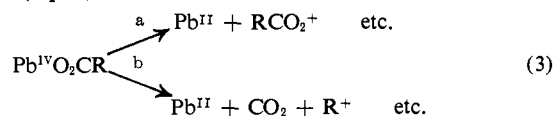
Lead tetraacetate¹ is a reagent widely applied in organic oxidations.² Mechanisms by which oxidation occurs are not completely established, and particularly germane is the nature of the Pb^{IV}-Pb^{II} transformation and the role of free radicals. We have chosen the oxidative decarboxylation of acids to examine these questions.

In an earlier study³ we demonstrated that oxidative decarboxylation of *n*-valeric, isovaleric, and 2-methylbutyric acids by Pb^{IV} acetate proceeded *via* a free-radical chain mechanism involving butyl radicals. The chain propagation sequence (eq 1 and 2) was proposed as an important part in this homolytic process.⁴



An alternative formulation for the mechanism of oxidative decarboxylation by Pb^{IV} is a nonchain process which denies alkyl radicals as vital intermediates. A variety of such heterolytic mechanisms has been presented to accommodate the formation of alkenes and esters. These mechanisms are distinguished from the radical chain sequence proposed above in that the Pb^{IV} carboxylate is considered to undergo a discrete

two-equivalent change from Pb^{IV} to Pb^{II}. For discussion here it is not pertinent whether such a direct Pb^{IV}-Pb^{II} transformation occurs *via* heterolysis of the ligand-Pb bond to form oxonium⁵ or carbonium ions⁶ (eq 3), or by a synchronous β elimination to form alkenes⁷ (eq 4).



The question of a homolytic or a heterolytic reaction has frequently remained unresolved because of the unequivocal observation of both radical and ionic characteristics in reactions of Pb^{IV} under differing conditions. Thus, a variety of functional groups other than carboxylic acids are readily oxidized by Pb^{IV} acetate. These include alcohols, glycols, alkenes, arenes, and various derivatives of amines. In a number of these cases, a step involving a direct Pb^{IV}-Pb^{II} has been speculatively included in the mechanism, and, indeed, a good case can be made for such two-equivalent processes.⁸

(5) W. Mosher and C. Kehr, *J. Am. Chem. Soc.*, 75, 3172 (1953).

(6) E. Corey and J. Casanova, Jr., *ibid.*, 85, 165 (1963).

(7) G. Buchi, R. Erickson, and N. Wakabayashi, *ibid.*, 83, 927 (1961).

(1) Hereafter referred to as Pb^{IV}.

(2) R. Criegee, "Oxidation in Organic Chemistry," K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter V.

(3) J. Kochi, *J. Am. Chem. Soc.*, 87, 3609 (1965).

(4) Except where it is pertinent to the discussion, no attempt will be made to include all of the coordination about the Pb atom.