sponding data previously published for 2,2-5,5-tetramethyl-THFD.[2] With the latter compounds the ϵ of the tetraalkyldioxolane, analogous to VII, indicates alcoholysis of the dioxolane ring in methanol.

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(2) C. Sandris and G. Ourisson, *Bull. Soc. Chim. France*, 338 (1958).

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY
EDWARD C. KENDALL
ZOLTAN G. HAJOS

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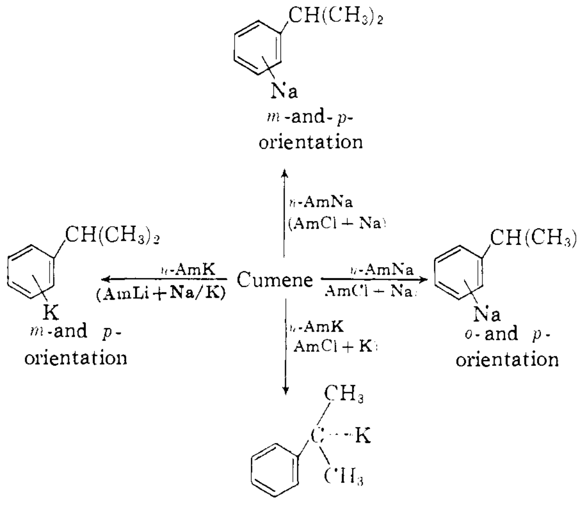
FACTORS GOVERNING ORIENTATION IN HETEROGENEOUS METALATION REACTIONS

Sir:

Compelling evidence has been advanced that *homogeneous* metalation reactions involve a nucleophilic attack by the anion of the metalating agent on hydrogen.[1] This view never has been generally accepted for heterogeneous metalations, particularly those involving organoalkali compounds,[2] although similarities between the two systems have been pointed out recently.[3,4]

Typical of the controversies which have prevailed in the area of heterogeneous metalations are the results which have been reported for the metalation of cumene by alkylalkali reagents. One laboratory[5,6] reports that *n*-amylsodium metalates cumene predominantly *para* and some *ortho* to the isopropyl group, while another[3] claims nearly a 1:1 *meta*/*para* ratio. Very little side chain metalation was observed with *n*-amylsodium by either Laboratory. *n*-Amylpotassium is reported to give almost exclusive side chain metalation, when the potassium reagent is prepared from *n*-amyl chloride and potassium,[7] but only 13% side chain product when it is prepared from *n*-amyllithium and a sodium-potassium alloy.[3]

An attempt[7] was made recently to explain these puzzling discrepancies on the basis that each Laboratory had prepared their organoalkali reagents by different methods. It was reasoned[7] that different modes of preparation would cause variations in the surfaces of these insoluble reagents and hence the metalations (which in all likelihood are surface reactions) might take different courses.



We are hereby reporting (see Table I) that *n*-amylsodium, prepared *either* from *n*-amyl chloride or di-*n*-amylmercury, metalates cumene almost entirely in the ring. Practically identical isomer distributions result in each case. Clearly the metal enters the ring in such fashion as to be as far removed from the isopropyl group as possible, which is contrary to findings in earlier reports.[5,6] We can only conclude that the *meta* isomer was not recognized as a major product by these earlier workers. Table I also discloses that when *n*-amylpotassium was prepared from both the chloride and di-*n*-amylmercury (entries 3 and 4) almost exclusive *alpha* metalation resulted. While the isomer ratios in the two cases were not identical they were extremely close. Further, if the metalation of cumene by *n*-amylpotassium in heptane was allowed to proceed for 20 hours, almost exclusive *alpha* metalation occurred (entry 5). If the reaction was interrupted at the end of 3 hours (entry 6), however, considerable quantities of *meta* and *para* isomer were found. *Clearly the latter two isomers disappear with time.* This is graphically illustrated by the results shown in Table II, wherein highly purified *p*-chlorocumene was treated with potassium in both excess

TABLE I

METALATION OF CUMENE BY *n*-AMYLSODIUM AND *n*-AMYLPOTASSIUM

	n-Amyl-	Prepn.	Solvent	% Isomer distribution[c,d,e] Alpha	Meta	Para
1	Na	*a*	Cumene	2.6	55.6	41.8
2	Na	*b*	Cumene	1.2	56.0	42.8
3	K	*a*	Cumene	88.0	4.5	7.5
4	K	*b*	Cumene	91.6	..	8.4
5	K	*a*	Heptane[f]	100		
6	K	*a*	Heptane[f,g]	42.0	39.0	19.0

[a] *n*-AmCl + metal. [b] *n*-Am$_2$Hg + metal. [c] All reactions were stirred at high speed at room temperature. [d] All analyses were of the methyl esters obtained by treating the carbonation products with excess diazomethane. Vapor phase chromatography was used in every case. [e] The reaction time was 20 hr. in every case except for entry 6. [f] Contained a two-mole excess of cumene. [g] The reaction time was 3 hr.

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(1) G. E. Hall, R. Piccolini and J. D. Roberts, THIS JOURNAL, **77**, 4540 (1955).

(2) A. A. Morton, *ibid.*, **69**, 969 (1947); see also A. A. Morton, *Chem. Revs.*, **35**, 1 (1944); A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955).

(3) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

(4) D. Bryce-Smith, V. Gold and D. P. N. Satchell, *ibid.*, 2743 (1954).

(5) A. A. Morton, J. T. Massengale and M. L. Brown, THIS JOURNAL, **67**, 1620 (1945).

(6) A. A. Morton and C. E. Claff, Jr., Abstracts of the 119th Meeting of the American Chemical Society, Boston, Mass., 1951, p. 11-M.

(7) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

cumene and heptane as a solvent. At the end of 20 hours, only the *alpha* product remained (entry 1).

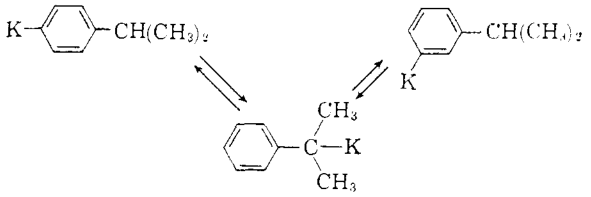
On the other hand, when the reaction was stopped after 4 hours, not only *alpha* product, but *meta* as well as *para* products were found (entry 2). *Meta* product again appeared when the reaction was carried out in heptane (entry 3). Clearly the data of Table II point to these equilibria in the presence of excess cumene.

TABLE II

REACTION OF HIGHLY PURIFIED *p*-CHLOROCUMENE WITH POTASSIUM

	Solvent	Reaction time, hr.	—% Isomer distribution— Alpha	Meta	Para
1	Cumene	20	100		
2	Cumene	4	60	23	17
3	Heptane[a]	5	56	20	24

[a] Contained a two-mole excess of cumene.



With time, the *alpha* isomer predominates because of its greater thermodynamic stability.

These findings provide a different explanation for the anomalous behavior of cumene in the presence of *n*-amylsodium and *n*-amylpotassium than has been presented by earlier workers.[3,7] According to the new picture, *both* reagents attack the ring of cumene first in a kinetically controlled sequence. The highly energetic *m*- and *p*-isopropylphenylpotassium thus formed equilibrate fairly rapidly to the more thermodynamically stable *alpha* isomer. The less energetic *m*- and *p*-isopropylphenylsodium, however, equilibrate at a negligible rate under the reaction conditions employed.

It is entirely possible that the rapid attainment of equilibrium with *n*-amylpotassium depends, among other things, upon the rate of stirring employed. Bryce-Smith[3] did not observe this equilibrium even with *p*-tolylpotassium at 20° for 40 days with "occasional shaking."[8] It seems certain that formation of benzylpotassium should be thermodynamically favored.[9] It remains for future work to determine why the establishment of these equilibria was so slow in the cases reported by Bryce-Smith.[3]

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DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA
ROBERT A. BENKESER
THOMAS V. LISTON

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BIS-3-METHYL-2-BUTYLBORANE AS A SELECTIVE REAGENT FOR STERIC CONTROL OF THE DIRECTION OF HYDROBORATION

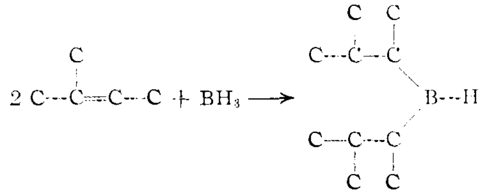
Sir:

The hydroboration of aliphatic terminal olefins proceeds to place the boron atom predominantly in the terminal position. Oxidation of the product provides a convenient route for the anti-Markownikoff hydration of the double bond.[1]

A detailed study of directive effects in this reaction[2] revealed that 1-hexene yields 94% 1-hexanol and 6% of 2-hexanol. Branching of the alkyl group, as in 3-methyl-1-butene and in 3,3-dimethyl-1-butene, does not alter the ratio of attack at the 1- and 2-positions. Similarly, *trans*-isopropylmethylethylene shows little discrimination between the two possible positions of the double bond: 43% 2-methyl-3-pentanol and 57% 4-methyl-2-pentanol. These results indicate that the direction of addition is determined primarily by electronic factors.

This conclusion is supported by the observation that styrene yields 20% of the α- and 80% of the β-isomer. A *p*-methoxy group changes this to 9% α- and 91% β-, whereas *p*-chloro changes this to 35% α-, 65% β-.

Hydroboration of 2-methyl-2-butene at 0° proceeds to the formation of bis-3-methyl-2-butylborane, even in the presence of excess olefin.



We have observed that this sterically hindered dialkylborane provides a measure of steric control of the hydroboration reaction and permits the synthesis of the less hindered alcohol in greatly improved purities.

Thus, hydroboration of 1-hexene by this reagent, followed by oxidation, yields 1-hexanol in a purity of at least 99%. Similarly, *trans*-isopropylmethylethylene yields 95% of the less hindered isomer, 4-methyl-2-pentanol. Both styrene and *p*-methoxystyrene yield the corresponding primary alcohols in purities of at least 98–99%.

Bis-3-methyl-2-butylborane is a readily prepared, highly valuable reagent for steric control of the direction of hydroboration.

A mixture of 80 ml. of diglyme, 23.1 g. (0.33 mole) of 2-methyl-2-butene, and 4.8 g. (0.125 mole) of sodium borohydride was cooled (ice bath), flushed with nitrogen, and treated with stirring with 23.6 g. (0.166 mole) of boron trifluoride etherate over a period of 0.5 hour. After standing for an additional hour at 0°, 20.1 g. (0.15 mole) of *p*-methoxystyrene (n^{20}D 1.5601) was added to the reaction mixture over a period of five minutes. The reaction was permitted to warm up to room temperature (approximately two hours) and then oxidized with alkaline peroxide, 50 cc. of a 3 *N* solu-

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(8) It is recognized that this reagent was prepared from *p*-tolyllithium which might well lead to an associated salt as the metalating agent with altered activity and properties. We are presently assessing this possibility as well as the effect of different stirring rates.

(9) H. Gilman, H. A. Pacevitz and O. Baine, THIS JOURNAL, **62**, 1514 (1940).

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(2) H. C. Brown and G. Zweifel, *ibid.*, in press.