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THE METALATION OF ALKANES BY ALKYLPOTASSIUM COMPOUNDS

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It has been found that butyl- and amylpotassium readily abstract hydrogen at room temperature from the *alkanes* pentane, hexane and cyclohexane. Metalation (metal-hydrogen interchange) brought about by means of sodium or potassium alkyls is a well known reaction in which hydrocarbons behave as weak protic acids.[1,2]

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[1] [a] G. E. Coates, *Organo-Metallic Compounds*, Methuen and Co., Ltd., London, 1960, p. 25, ff. [b] E. G. Rochow, D. T. Hurd and R. N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 68, ff. [c] R. A. Benkeser, D. J. Foster, D. M. Sauve and J. F. Nobis, *Chem. Rev.* *57*, 867 (1957). [d] E. J. Lanpher, L. M. Redman and A. A. Morton, *J. Org. Chem.* *23*, 1370 (1958). [e] R. A. Finnegan and R. S. McNees, *Chemistry and Industry* 1450 (1961). [f] R. A. Finnegan and R. S. McNees, *Tetrahedron Letters* 755 (1962).

[2] In addition to metalation, by which we imply a stoichiometric hydrogen-metal interchange, base *catalyzed* hydrogen exchange reactions of hydrocarbons are well established.[2a-h] [a] A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *J. Am. Chem. Soc.* 84, 3164 (1962). [b] A. Schriesheim and C. A. Rowe, Jr., *ibid.* *84*, 3160 (1962). [c] R. E. Dessey, Y. Okuzumi and A. Chen, *ibid.* *84*, 2899 (1962). [d] A. Streitwieser et al., *ibid.* *84*, 244, *249*, *251*, 254, 258 (1962). [e] H. Pines and L. A. Schaap, *Advances in Catalysis XII*, 117 (1960). [f] A. I. Shatenshtein, *Tetrahedron* *18*, 95 (1962). [g] A. I. Shatenshtein and L. N. Vasilyeva, *Proc. Acad. Sci. USSR* *85*, No. 1, 115 (1954). [h] A. I. Shatenshtein, L. N. Vasilyeva, N. M. Dykhno, and E. A. Izrailevich, *ibid.* *85*, No. 2, 381 (1952).

In general, two types of acidic hydrocarbons have been discerned: a) those giving rise to resonance stabilized conjugate bases, e.g. toluene and propylene in which a benzylic or allylic hydrogen may be removed with the formation of the benzyl or allyl carbanion; and b) those in which the conjugate base is not resonance stabilized but whose C-H bond orbitals have increased *s* character, e.g., acetylene (*sp*), ethylene and benzene (sp^2) and cyclopropane ($sp^{2.28}$).[3,4] The metalation of alkanes (Equation 1, R and R' = saturated alkyl groups)

$$(1)\quad RM + R'H \rightleftarrows RH + R'M$$

has not been previously reported.[5,5a] In the present experiments a solution of dialkyl mercury compound (0.05 mole) in 40 ml. solvent was slowly added to a suspension of potassium sand (0.11 g. atom) in ca. 200 ml. solvent under the influence of high speed stirring, a temperature of 10° and a helium atmosphere. After the addition was complete (1 - 1½ hr.), the reaction mixture was allowed to warm to 25-30° and high speed stirring was maintained for an additional 1 - 2 hours. The contents of the flask were then transferred to a

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[3] L. L. Ingraham in M. S. Newman, *Steric Effects in Organic Chemistry* John Wiley and Sons, Inc., New York, (1956), p. 518.

[4] For the metalation of cyclopropanes: [a] E. J. Lanpher, L. M. Redmen and A. A. Morton, *J. Org. Chem.* 23, 1370 (1958). [b] R. A. Finnegan, *Tetrahedron Letters* in press, (1962). [c] R. A. Finnegan, R. S. McNees and A. W. Hagen, unpublished experiments.

[5] Schatenshtein[2g,h] has reported hydrogen-deuterium exchange experiments with alkanes and deuterated potassium amide under drastic conditions; heptane acquires 2-3 atoms of deuterium when the reagents are agitated at 120° for 140-500 hours.

[5a] Although the incursion of free radical steps might be invoked in part to explain the present results, a polar interpretation is favored at the present time in view of its simplicity and close analogy with the past literature.

bottle and diluted to 300 ml. with additional solvent. At this point the first analysis was made by evaporating an aliquot with a helium stream followed by pumping on the residue for 3 to 7 hours at approximately 0.1 mm. (25-30°) to insure complete removal of the solvent. The residual solid mixture of mercury and potassium salts was then hydrolyzed to produce hydrocarbons which were expanded into a gas burette at atmospheric pressure. The hydrocarbons so produced were analyzed by gas chromatography[6] and the results of analyses at different times after preparation of the reagents are summarized in the accompanying table. The figures given in the table represent percentage composition of the hydrocarbon vapors and are a reflection[7] of the composition of the organometallic aggregate.

It can be seen that the organopotassium reagent actually obtained when butylpotassium is prepared in pentane or hexane as the "inert" suspending medium consists to a significantly large extent of organopotassium compounds derived from the solvent. These data demonstrate for the first time that hydrogen-metal interchange occurs in completely saturated systems with some facility. Even cyclohexane which contains all secondary hydrogens, is metalated by butyl- and amylpotassium to a surprising extent. As expected, however, the reaction with cyclohexane occurs to a markedly lesser

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[6] The analytical method establishes the skeleton of any organopotassium reagent in the mixture (i.e. the hydrocarbon from which it is derived) and does not permit location of the metal atom in the molecule nor does it preclude the presence of polymetalated species.

[7] The experimental technique discriminates against the less volatile components of the hydrocarbon mixture; accordingly, the figures are considered to have at best semi-quantitative significance. These details will be discussed in a full paper.

TABLE

METALATION OF ALKANES

Reactants	Products	Same Day	After 24 hours	After 1 week
$(C_4H_9)_2Hg$ + K	Total % C_4	58	14	10
in pentane	Total % C_5	35	50	62
$(C_4H_9)_2Hg$ + K	Total % C_4	56	37	49
in hexane	Total % C_6	40	57	30
$(C_4H_9)_2Hg$ + K	Total % C_4	78	49	48
in cyclohexane	Total % cyclic C_6	6	32	33
$(C_5H_{11})_2Hg$ + K	Total % C_5	81	39	37
in cyclohexane	Total % cyclic C_6	12	36	37

extent than the reactions with pentane and hexane suggesting in the latter cases that most of the metalation occurs at the primary carbons of the methyl groups. The differences in the data for butylpotassium in pentane and in hexane as the reaction progresses may be in part[7] explained by the higher concentration of methyl groups in pentane (17.4 N) than in hexane (15.7 N) as well as by the fact that C_4 species may be derived from C_6 species by fragmentation.

It will be noted that the percentage composition of the products in a given experiment does not total 100%. These differences (from 100%) represent mainly fragmentation products (i.e. C_1, C_2 and C_3 hydrocarbons) as well as some unidentified species. Furthermore, it should be emphasized that the entries in the table represent the total hydrocarbon with the carbon skeleton specified in the second column. In every case this total comprises not only the saturated but also all of the corresponding unsaturated species which are derived by metal hydride elimination and metalation of the resultant olefin to give unsaturated organopotassium compounds. These additional complicating features of these reaction systems, i.e. fragmentation by carbon-carbon cleavage and hydride elimination by carbon-hydrogen cleavage, are discussed in an accompanying communication. Additional studies may be expected to uncover new and significant features of carbanion reactivity and hydrocarbon acidity.

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